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The Impact of the Congestion Charging Scheme on Air Quality in London

Part 1. Emissions Modeling and Analysis of Air Pollution Measurements

Part 2. Analysis of the Oxidative Potential of Particulate Matter

Frank Kelly, H. Ross Anderson, Ben Armstrong, Richard Atkinson,
Ben Barratt, Sean Beevers, Dick Derwent, David Green,
Ian Mudway, and Paul Wilkinson

Includes a Commentary by the Institute's Health Review Committee

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ABOUT HEI

The Health Effects Institute is a nonprofit corporation chartered in 1980 as an independent research organization to provide high-quality, impartial, and relevant science on the effects of air pollution on health. To accomplish its mission, the institute

- Identifies the highest-priority areas for health effects research;
- Competitively funds and oversees research projects;
- Provides intensive independent review of HEI-supported studies and related research;
- Integrates HEI's research results with those of other institutions into broader evaluations; and
- Communicates the results of HEI's research and analyses to public and private decision makers.

HEI receives half of its core funds from the U.S. Environmental Protection Agency and half from the worldwide motor vehicle industry. Frequently, other public and private organizations in the United States and around the world also support major projects or certain research programs. HEI has funded more than 280 research projects in North America, Europe, Asia, and Latin America, the results of which have informed decisions regarding carbon monoxide, air toxics, nitrogen oxides, diesel exhaust, ozone, particulate matter, and other pollutants. These results have appeared in the peer-reviewed literature and in more than 200 comprehensive reports published by HEI.

HEI's independent Board of Directors consists of leaders in science and policy who are committed to fostering the public–private partnership that is central to the organization. The Health Research Committee solicits input from HEI sponsors and other stakeholders and works with scientific staff to develop a Five-Year Strategic Plan, select research projects for funding, and oversee their conduct. The Health Review Committee, which has no role in selecting or overseeing studies, works with staff to evaluate and interpret the results of funded studies and related research.

All project results and accompanying comments by the Health Review Committee are widely disseminated through HEI's Web site (*www.healtheffects.org*), printed reports, newsletters and other publications, annual conferences, and presentations to legislative bodies and public agencies.

ABOUT THIS REPORT

Research Report 155, *The Impact of the Congestion Charging Scheme on Air Quality in London: Part 1. Emissions Modeling and Analysis of Air Pollution Measurements*, and *Part 2. Analysis of the Oxidative Potential of Particulate Matter,* presents a research project funded by the Health Effects Institute and conducted by Professor Frank Kelly, of the School of Biomedical Sciences, King's College London, London, U.K., and his colleagues. This report contains three main sections.

The HEI Statement, prepared by staff at HEI, is a brief, nontechnical summary of the study and its findings; it also briefly describes the Health Review Committee's comments on the study.

The Investigators' Report, Parts 1 and 2, prepared by Kelly and colleagues, describes the scientific background, aims, methods, results, and conclusions of the study.

The Commentary is prepared by members of the Health Review Committee with the assistance of HEI staff; it places the study in a broader scientific context, points out its strengths and limitations, and discusses remaining uncertainties and implications of the study's findings for public health and future research.

This report has gone through HEI's rigorous review process. When an HEI-funded study is completed, the investigators submit a draft final report presenting the background and results of the study. This draft report is first examined by outside technical reviewers and a biostatistician. The report and the reviewers' comments are then evaluated by members of the Health Review Committee, an independent panel of distinguished scientists who have no involvement in selecting or overseeing HEI studies. During the review process, the investigators have an opportunity to exchange comments with the Review Committee and, as necessary, to revise their report. The Commentary reflects the information provided in the final version of the report.

PREFACE

HEI's Outcomes Research Program

The goal of most air quality regulations is to protect the public's health by implementing regulatory actions or providing economic incentives that help reduce the public's exposure to air pollutants. If this goal is met, air pollution should be reduced, and indicators of public health should improve or at least not deteriorate. Evaluating the extent to which air quality regulations succeed in protecting public health is part of a broader effort — variously termed outcomes research, accountability research, or research on regulatory effectiveness — designed to assess the performance of environmental regulatory policies in general. In recent decades, air quality in the United States and Western Europe has improved substantially, and this improvement is attributable to a number of factors, including increasingly stringent air quality regulations. However, the cost of the pollution-control technologies and mechanisms needed to implement and enforce these regulations is often high. It is therefore prudent to ask whether the regulations have in fact yielded demonstrable improvements in public health and provided information to inform future efforts to do so.

Several U.S. government agencies have concluded that direct evidence about the extent to which air quality regulations have improved health (measured as a decrease in premature mortality and excess morbidity) is lacking. This finding is well documented by the National Research Council (NRC) in its report Estimating the Public Health Benefits of Proposed Air Pollution Regulations (NRC 2002), as well as by the California Air Resources Board, the U.S. Environmental Protection Agency (EPA), the U.S. Centers for Disease Control and Prevention (CDC), and other agencies.

In 2003, the Health Effects Institute published a monograph on outcomes research, Communication 11, Assessing Health Impact of Air Quality Regulations: Concepts and Methods for Accountability Research (HEI 2003). This monograph was written by the members of HEI's multidisciplinary Accountability Working Group after a 2001 workshop on the topic. Communication 11 set out a conceptual framework for outcomes research and identified the types of evidence required and the methods by which the evidence should be obtained. It has also guided the development of the HEI Health Outcomes Research program, which is discussed below.

Between 2002 and 2004, HEI issued four requests for applications (RFAs) for studies to evaluate the effects of actions taken to improve air quality. The study by Professor Frank Kelly and colleagues described in this Research Report (Kelly et al. 2011a,b) was funded under RFA 04-1, "Measuring the Health Impacts of Actions That Improve Air Quality." HEI funded eight additional outcomes studies resulting from other RFAs.

This preface describes both the framework of outcomes research as it relates to air quality regulations and HEI's Outcomes Research program.

BACKGROUND

The first step in assessing the effectiveness of air quality regulations is to measure emissions of the targeted pollutants to see whether they have in fact decreased as intended. A series of intermediate assessments, described in detail below, are needed in order to accurately measure the adverse health effects associated with air pollution to see whether they, too, decreased in incidence or severity relative to emissions. Some outcomes studies to date have used hypothetical scenarios (comparing estimated outcomes under existing and more stringent regulations) and risk estimates obtained from epidemiologic studies in an attempt to quantify past effects on health and to predict future effects (U.S. EPA 1999). However, more extensive validation of these estimates with data on actual outcomes would be helpful.

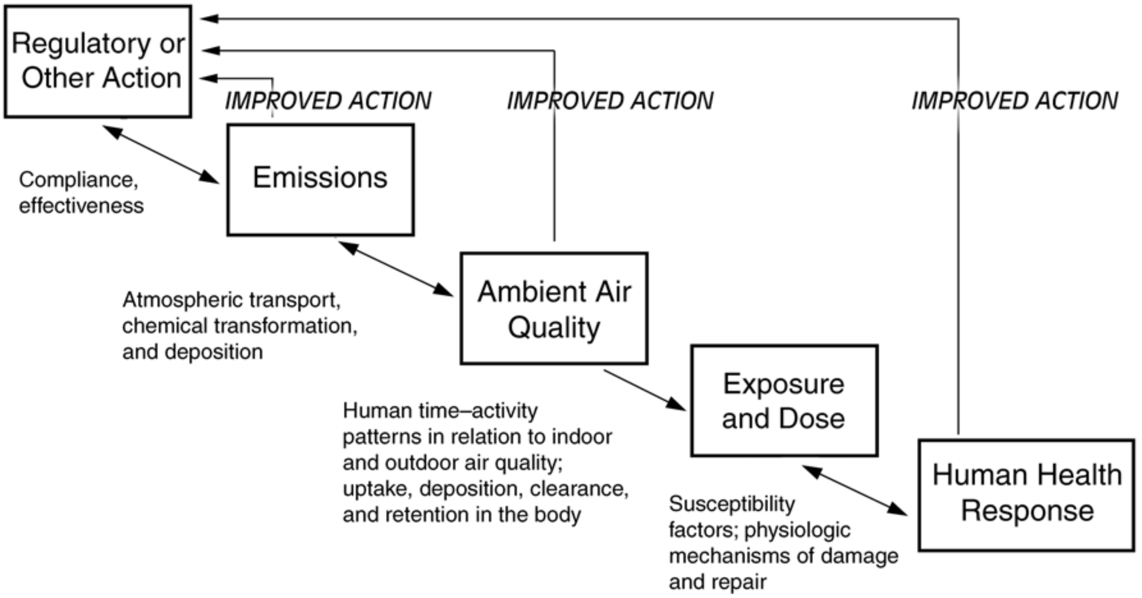
The long-term improvements in U.S. air quality have been associated with improved health in retrospective epidemiologic studies (Chay and Greenstone 2003; Laden et al. 2006; Pope et al. 2009). Considerable challenges, however, are inherent in the assessment of the health effects of air quality regulations. Different regulations go into effect at different times, for example, and may be implemented at different levels of government (e.g., national, regional, or local). Their effectiveness therefore needs to be assessed in ways that take into account the varying times of implementation and levels of regulation. In addition, other changes at the same time and place might confound an apparent association between pollution reduction and improved health, such as economic trends (e.g., changes in employment), improvements in health care, and behavioral changes (e.g., staying indoors when government warnings indicate pollution concentrations are high). Moreover, adverse health effects that might be caused by exposure to air pollution can also be caused by other environmental risk factors (some of which may have changed over the same time periods as the air pollution concentrations). These challenges become more pronounced when regulations are implemented over long periods and when changes in air quality and health outcomes are not seen immediately, thus increasing the chance for confounding by other factors. For these reasons, scenarios in which regulations are expected to have resulted in rapid changes in air quality tend to be among the first, and most likely, targets for investigation, rather than evaluations of complex regulatory programs implemented over multiple years. Studies in Ireland by Clancy and colleagues (2002) and in Hong Kong by Hedley and colleagues (2002) are examples of such scenarios.

These inherent challenges are well documented in Communication 11 (HEI 2003), which was intended to advance the concept of outcomes research and to foster the development of methods and studies throughout the relevant scientific and policy communities. In addition, recent advances in data collection and analytic techniques provide an unprecedented opportunity to improve our assessments of the effects of air quality interventions.

THE OUTCOMES EVALUATION CYCLE

The NRC's Committee on Research Priorities for Airborne Particulate Matter set out a conceptual framework for linking air pollution sources to adverse health effects (NRC 1998). This framework can be used to identify factors along an Outcomes Evaluation Cycle (see Preface Figure), each stage of which affords its own opportunities for making quantitative measurements of the intended improvements.

At the first stage (regulatory action), one can assess whether controls on source emissions have in fact been put into place. At the second stage (emissions), one can



Outcomes Evaluation Cycle. Each box represents a stage in the process between regulatory action and human health responses to air pollution. Arrows connecting the stages indicate possible directions of influence. The text below the arrows identifies factors affecting the effectiveness of regulatory actions at each stage. At several of the stages, knowledge gained from studies on outcomes can provide valuable feedback for improving regulatory or other actions.

determine whether controls on sources have indeed reduced emissions, whether emitters have changed their practices, and whether there have been unintended consequences. At the third stage (ambient air quality), one can assess whether controls on sources and reductions in emissions have resulted in improved air quality. At the fourth stage (personal or population exposure), one can assess whether the improvement in air quality has reduced people's actual exposure and whether susceptible subpopulations (those most likely to experience adverse health effects) have benefited. At this stage, it is important to take into account changes in time–activity patterns that could either increase or reduce exposure. The actual dose that an individual's organs may be exposed to should also be considered (i.e., whether reductions in exposure have led to reductions in concentrations in body tissues such as the lung). Finally, at the fifth stage (human health response), one can assess whether risks to health have declined, given the evidence about changes in health outcomes such as morbidity and mortality that have resulted from changes in exposure. The challenge at this stage is to investigate the health outcomes that are most directly related to exposure to air pollution.

At each stage in the outcomes evaluation cycle, the opportunity exists to collect evidence that either validates the assumptions that motivated the intervention or points to ways in which the assumptions were incorrect. The collection of such evidence can thus ensure that future interventions are maximally effective.

Ultimately, the framework for outcomes research will need to encompass investigations of the broader consequences of regulations, not just the intended consequences. Unintended consequences should also be investigated, along with the possibility that risks to public health in fact increased, as discussed by Wiener (1998) and others who have advanced the concept of a portfolio of effects of a regulation.

HEI'S OUTCOMES RESEARCH PROGRAM

HEI's Outcomes Research program currently includes nine studies. The study by Professor Frank Kelly and colleagues presented in this report is the third of the nine to be published; four additional studies are in press and are expected to be published in 2011. The remaining two studies are in review and are expected to be published in 2012.

These studies involve the measurement of indicators along the entire outcomes evaluation cycle, from regulatory or other interventions to human health outcomes. Some of the studies focused on interventions that are implemented over relatively short periods of time, such as a ban on the sale of coal, the replacement of old wood stoves with more efficient, cleaner ones, reductions in the sulfur content of fuels, and measures to reduce traffic. Other groups focused on longer-term, wider-ranging interventions or events; for instance, one study assessed complex changes associated with the reunification of the former East and West Germany, including a switch from brown coal to natural gas for fueling power plants and home-heating systems and an increase in the numbers of modern diesel-powered vehicles in eastern Germany. HEI is also supporting research, including the development of methods, in an especially challenging area — the effects of regulations that are implemented incrementally over extended periods of time, such as those resulting from Title IV of the 1990 Clean Air Act Amendments (U.S. EPA 1990), which aimed at reducing sulfur dioxide emissions from power plants by requiring compliance with prescribed emission limitations. Studies on health outcomes funded by HEI to date are summarized in the Preface Table and described in more detail in an interim evaluation of the HEI Outcomes Research program (van Erp and Cohen 2009).

FUTURE DIRECTIONS

As a part of its new Strategic Plan for 2010 through 2015 (HEI 2010a), HEI has looked closely at opportunities for unique new contributions to health outcomes research. Key recommendations for future research were made at a December 2009 planning workshop (HEI 2010b), which led to HEI issuing a new Request for Applications in January 2011 for a second wave of outcomes research. RFA 11-1, "Health Outcomes Research — Assessing the Health Outcomes of Air Quality Actions," solicits applications for studies designed to assess the health effects of actions to improve air quality and to develop methods required for, and specifically suited to, conducting such research. Preference will be given to (1) studies that evaluate regulatory and other actions at the national or regional level implemented over multiple years; (2) studies that evaluate complex sets of actions targeted at improving air quality in large

HEI's Outcomes Research Program[a]

RFA / Investigator (Institution)	Study or Report Title	Intervention
RFA 02-1		
Douglas Dockery (Harvard School of Public Health, Boston, Mass.)	"Effects of Air Pollution Control on Mortality and Hospital Admissions in Ireland" (in review)	Coal ban in Irish cities
Annette Peters (GSF–National Research Center for Environment and Health, Neuherberg, Germany[b])	The Influence of Improved Air Quality on Mortality Risks in Erfurt, Germany (published as HEI Research Report 137, 2009)	Switch from brown coal to natural gas for home heating and power plants, changes in motor vehicle fleet after reunification of Germany
RFA 04-1		
Frank Kelly (King's College London, London, U.K.)	The Impact of the Congestion Charging Scheme on Air Quality in London: Part 1. Emissions Modeling and Analysis of Air Pollution Measurements. Part 2. Analysis of the Oxidative Potential of Particulate Matter (published as HEI Research Report 155, 2011)	Measures to reduce traffic congestion in the center of London
RFA 04-4		
Frank Kelly (King's College London, London, U.K.)	"The London Low Emission Zone Baseline Study" (in press)	Measures to exclude most polluting vehicles from entering Greater London
Richard Morgenstern (Resources for the Future, Washington, D.C.)	"Accountability Assessment of Title IV of the Clean Air Act Amendments of 1990" (in press)	Measures to reduce sulfur emissions from power plants east of the Mississippi River
Curtis Noonan (University of Montana, Missoula, Mont.)	"Assessing the Impact on Air Quality and Children's Health of Actions Taken to Reduce $PM_{2.5}$ Levels from Woodstoves" (in press)	Woodstove change-out program
Jennifer Peel (Colorado State University, Fort Collins, Colo.)	Impact of Improved Air Quality During the 1996 Summer Olympic Games in Atlanta on Multiple Cardiovascular and Respiratory Outcomes (published as HEI Research Report 148, 2010)	Measures to reduce traffic congestion during the Atlanta Olympics
Chit-Ming Wong (University of Hong Kong, Hong Kong)	"Impact of the 1990 Hong Kong Legislation for Restriction on Sulfur Content in Fuel" (in press)	Measures to reduce sulfur content in fuel for motor vehicles and power plants
RFPA 05-3		
Junfeng (Jim) Zhang (University of Medicine and Dentistry of New Jersey, Piscataway, N.J.)	"Molecular and Physiological Responses to Drastic Changes in PM Concentration and Composition" (in review)	Measures to improve air quality during the Beijing Olympics

[a] Abbreviations: RFA, Request for Applications; RFPA, Request for Preliminary Applications.

[b] As of 2008, this institution is called the Helmholtz Zentrum München–German Research Center for Environmental Health.

urban areas and major ports with well-documented air quality problems and programs to address them; and (3) studies that develop methods to support such health outcomes research (see *www.healtheffects.org/funding.htm*). HEI hopes to fund 3 or 4 studies to evaluate the effectiveness of longer-term regulatory actions that are expected to start in 2012.

In addition, HEI has also funded the development of two Web sites intended to enhance transparency and provide other researchers with access to extensive data and software from HEI-funded studies:

1. Data and software from the National Morbidity, Mortality, and Air Pollution Study (NMMAPS), as described by Zeger and colleagues (2006) (data available at the Johns Hopkins Bloomberg School of Public Health Web site *www.ihapss.jhsph.edu*); and
2. Data from the National Particle Components Toxicity Initiative (NPACT) on concentrations of components of particulate matter with an aerodynamic diameter ≤ 2.5 µm ($PM_{2.5}$) collected at or near the 54 sites in the EPA's $PM_{2.5}$ Chemical Speciation Trends Network (STN) (data available at the Atmospheric and Environmental Research, Inc., Web site *http://hei.aer.com*).

The data on pollution and health from a large number of U.S. cities, as documented by the NMMAPS team and made available on the Internet-Based Health and Air Pollution Surveillance System (iHAPSS) Web site, constitute a valuable resource that allows other researchers to undertake additional analyses, possibly including further outcomes studies. The STN Web site provides scientists an opportunity to investigate specific questions about concentrations of $PM_{2.5}$ components and their association with adverse health effects in regions covered by the STN network and to address questions related to outcomes research when interventions in these regions are being planned.

In January 2008, HEI co-organized and cosponsored, with the CDC's Environmental Public Health Tracking Program and the EPA, a workshop entitled "Methodologic Issues in Environmental Public Health Tracking of Air Pollution Effects." The workshop was part of an effort to implement the initiative outlined in HEI's Strategic Plan for 2005 through 2010 (HEI 2005) to "build networks with the U.S. Centers for Disease Control and Prevention and state public health tracking programs to facilitate accountability research."

The workshop built on the work of the CDC's Environmental Public Health Tracking Program (see the CDC Web site *www.cdc.gov/nceh/tracking/*) in the development of standardized measures of air pollution–related effects on health at the state and local levels in the United States. It brought together representatives of state and federal agencies and academic researchers to discuss methodologic issues in developing standardized measures and made recommendations for their further development and application in assessing the health impacts of air pollution, including the impacts of actions taken to improve air quality. The recommendations were provided in a September 2008 report to the CDC, and the proceedings were published in the journal *Air Quality, Atmosphere & Health* in December 2009 (e.g., Matte et al. 2009). The CDC has subsequently funded a pilot project under the Environmental Public Health Tracking Program to implement the recommendations of the workshop in selected states and metropolitan areas.

HEI will continue to seek opportunities to work with the CDC and the EPA to apply methods newly developed for tracking public health to the assessment of the effectiveness of environmental regulations.

Investigators who have identified a distinctive opportunity to evaluate the effects of environmental regulations on air pollution and human health are encouraged to contact HEI.

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HEI STATEMENT

Synopsis of Research Report 155

The Congestion Charging Scheme and Air Quality in London

INTRODUCTION

The study of the London Congestion Charging Scheme (CCS), conducted by Professor Frank Kelly and colleagues, was funded under HEI's research program aimed at measuring the possible health impacts associated with actions taken to improve air quality. With this research program, HEI has sought to (1) fund studies to assess the health outcomes associated with regulatory and incentive-based actions to improve air quality at local or national levels, and (2) develop methods required for, and specifically suited to, conducting such research.

The CCS offered an unusual opportunity to investigate the potential impact on air quality of a discrete and well-defined intervention to reduce traffic congestion in the middle of a major city. The CCS was implemented in London in February 2003 with the primary aim of reducing traffic congestion by charging vehicles to enter the central part of London, defined as the congestion charging zone (CCZ). In an earlier study based on data from the first year of the scheme, members of the investigative team had reported early findings of modest reductions in the number of vehicles entering the zone and had projected declines of about 12% in emissions of both PM_{10} (particulate matter with an aerodynamic diameter of ≤ 10 µm) and nitrogen oxides (NO_x) within the CCZ. Recognizing that these projected reductions, coupled with the small area represented by the CCZ within Greater London, could lead to relatively small changes in air quality, the HEI Health Research Committee recommended that the investigators first assess the actual changes in air quality and postpone their proposal to study health impacts until the air quality studies were completed. The investigators proposed a multifaceted approach to exploring the impact of the CCS on air quality, which involved a variety of modeling techniques, analysis of air monitoring data, and a newly developed assay for the oxidative potential of PM.

STUDY METHODS

Kelly and his colleagues undertook a stepwise approach to evaluating the impact of the CCS on air quality. In the first part of their study, they updated emission estimates that had originally been developed for the London transportation agency, Transport for London. Using the King's College London Emissions Toolkit (a set of statistical models and data), they developed detailed estimates of NO_x, nitrogen dioxide (NO_2), and PM_{10} emissions from vehicular and non-vehicular sources throughout the London area for the 4-year period encompassing 2 years before (pre-CCS) and 2 years after (post-CCS) the introduction of the scheme on February 17, 2003. Vehicular PM_{10} emissions were predicted from two primary sources — tire and brake wear and exhaust. These emission estimates were then input to a modeling system (the King's College London Air Pollution Toolkit), which the investigators used to predict annual mean ambient concentrations of NO_x, NO_2, and PM_{10} throughout London for each year of the study. They explored how various assumptions about the mix of vehicles, speed, and congestion over the study period might affect the predicted spatial patterns of changes in air quality associated with the implementation of the CCS.

The results of the modeling exercise were also used to help select the fixed, continuous air monitoring sites from the London Air Quality Network (LAQN) with which to evaluate measured changes in air quality. The investigators created a CCS Study Database consisting of validated (or ratified) measurements of carbon monoxide (CO), nitric oxide (NO), NO_2, NO_x, and PM_{10} from monitors sited to record roadside or urban or suburban background air pollutants across London. The investigators calculated and compared geometric mean concentrations of these pollutants for the 2 years before (2001–2002) and 2 years after (2003–2004) the scheme was

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This Statement, prepared by the Health Effects Institute, summarizes a research project funded by HEI and conducted by Professor Frank J. Kelly at the School of Biomedical Sciences, King's College London, U.K., and colleagues. Research Report 155 contains both the detailed Investigators' Report and a Commentary on the study prepared by the Institute's Health Review Committee.

introduced. The changes over time at monitors within the zone were compared with changes during the same period at similar classes of monitoring sites in a control area more than 8 km from the center of the zone. In addition, the investigators also explored three other analytic techniques for characterizing and evaluating both projected and measured changes in pollutant concentrations over the period of the study: ethane as an indicator of pollutant dispersion due to regional atmospheric conditions; the cumulative sum statistical technique to identify step changes in air pollution data; and specialized graphical techniques to improve the siting of pollutant monitors by characterizing the dependence of pollutant concentrations at potential monitoring sites on local emission sources.

In the second part of the study, the investigators set out to explore whether implementation of the CCS led to detectable changes in either the composition of the PM_{10} mixture or in its oxidative potential — an indicator of toxicity. As part of this analysis, they sought to establish a more comprehensive baseline of monitoring data to use in future studies of the CCS by collecting data from additional monitoring sites located within and outside a proposed expansion of the CCZ known as the Western Extension.

For these purposes, the investigators created an archive of about 730 filters from tapered element oscillating microbalances, a type of PM_{10} monitor used at 16 sites within and surrounding the CCZ, including the Western Extension; the filter archive covered the 3 years before and 3 years after the CCS was introduced. After extracting the PM from the filters, they measured the oxidative potential of the extracts using an in vitro assay that measures the ability of the extracts to deplete antioxidants in a synthetic respiratory tract lining fluid. The investigators' focus on oxidative potential, a measure of the capacity to generate oxidation reactions, arises from a leading theory about the causal role that oxidative stress may play in the health effects associated with exposure to air pollution. Their goal, in essence, was to use oxidative potential as an indicator of the potential toxicity of PM and to evaluate how it varied across London and in response to the introduction of the CCS.

To study the composition of PM, each filter extract was also analyzed using inductively coupled plasma mass spectrometry for a panel of metals that have been associated with traffic sources in studies by other investigators. Additional experiments were done to understand the relative contribution of different metal and non-metal components of PM to the oxidative potential measured in the assays.

RESULTS AND INTERPRETATION

The modeling studies predicted small changes in both emissions and ambient concentrations of NO_x, NO_2, and PM_{10} across London that could be related to the implementation of the CCS, although the effects within the CCZ were projected to be more pronounced than elsewhere. They projected somewhat larger average reductions (about 20%) in NO_x and PM_{10} emissions than the 12% reductions that had been predicted in the initial feasibility studies that preceded the CCS. However, the difference in these projections may partly be explained by the fact that the modeling in this study compared the 2 years before and 2 years after the introduction of the CCS, whereas the earlier estimates had been based on an analysis of only the first year of the scheme (2003). The investigators reported that unusual meteorologic conditions had led to periods of elevated pollution levels in London during that year.

Despite the somewhat larger projected reductions in emissions, the projected changes in concentrations of NO_x, NO_2, and PM_{10} related to the CCS were small. Within the CCZ, the investigators projected a net decline of 1.7 ppb in the annual average mean NO_x concentration and a decline of 0.8 $\mu g/m^3$ in PM_{10}. The modeling also suggested that a major proportion of PM_{10} might be accounted for by regional background levels, but that contributions from tire and brake wear might also be important. NO_2 was projected to increase slightly, by 0.3 ppb on average; the investigators attributed this increase to higher NO_2 emissions associated with the introduction of particle traps on diesel buses as part of Transport for London's improvements in the public transport system.

From their comparison of actual air pollutant measurements within the CCZ with those at control sites in Outer London, the investigators reported little evidence of CCS-related changes in pollutant levels at roadside monitoring sites, where their modeling had suggested the most pronounced effects would be seen. The effects of the CCS were more evident at urban background sites within the CCZ when compared with concentrations at sites in the control area: PM_{10} concentrations declined by

12% at the one background site in the CCZ where it was measured, and NO declined by between 10% and 25% at the three background sites where it was measured. However, levels of NO_2 increased by between 2% and 20% at the three background sites compared with levels at the control sites; these increases were consistent with the predictions from the modeling studies and with the likely effects of the parallel intervention that introduced more filter-equipped diesel buses. The investigators concluded that the small net changes in NO_x detected at both roadside and background monitoring sites — likely resulting from reductions in NO offset by increases in NO_2 — did not provide strong evidence of an impact of the CCS.

In the study of the oxidative potential of PM_{10}, the investigators were unable to identify a temporal, CCS-related change during the 6-year period that encompassed the implementation of the scheme. However, the city-wide spatial analysis of oxidative potential revealed that PM_{10} sampled from roadside locations showed greater oxidative activity than PM_{10} sampled at urban background sites.

When they coupled these spatial analyses of oxidative potential with analyses of the metal content of PM_{10} from the same filters, the investigators concluded that their results provided suggestive evidence that PM_{10} derived from tire and brake wear (indicated by the presence of the metals arsenic, barium, copper, iron, manganese, nickel, and vanadium) might contribute to the oxidative potential of PM seen in filters from roadside monitoring sites. However, the investigators noted that correlations among the concentrations of PM_{10} attributed to exhaust and to tire and brake wear made it difficult to isolate how much these individual sources might contribute to the oxidative potential of PM_{10}. Their other experimental findings suggested that the non-metal components of PM_{10} did not contribute substantially to oxidative potential in this assay, but the investigators could not rule out a role for all other non-metal components of ambient air pollution.

Overall, the investigators concluded that their primary and exploratory analyses collectively suggested that the introduction of the CCS in 2003 was associated with small temporal changes in air pollutant concentrations within the CCZ compared with those in control areas thought to be beyond the influence of the scheme. In addition, they observed that a number of limitations, including concurrent changes in transportation and emission control policies, unusual meteorologic conditions the year the scheme was introduced, and the influence of strong local sources on particular monitors, would preclude them from attributing these changes to the CCS alone. They also acknowledged that the area covered by the CCS — approximately 1.4% of Greater London — was likely too small to influence air pollutant levels substantially either within or outside the zone.

CONCLUSIONS AND IMPLICATIONS

In its independent evaluation of the study, the HEI Health Review Committee thought that Kelly and his colleagues made a laudable effort to evaluate the scheme's impact. The team undertook a creative, stepwise, multidisciplinary approach beginning with updated modeling of potential changes in emissions and air pollutant concentrations, followed by multiple approaches to the analysis of actual air monitoring data. They demonstrated the value of a careful modeling approach before decisions are made about whether and how to undertake studies of the actual impacts of air quality interventions, including insights as to where monitoring networks might best be positioned to capture the impact of a traffic-reduction scheme.

However, the investigators encountered a set of issues that have come to exemplify the general challenges posed by studies of this kind. One is simply the difficulty of detecting significant air quality improvements related to an intervention against the backdrop of broader regional and meteorologic changes in the background concentrations of pollutants. A second is that other changes occurring at the same time (e.g., the introduction of more filter-equipped diesel buses in response to a separate rule) may also affect air quality and obscure effects of the intervention being studied. A third is that institutional or behavioral changes in response to an intervention, not all of which may be fully anticipated, can also partly offset the possible gains expected. Finally, their experience highlights the challenges of using existing monitoring networks, even one as well-established as the LAQN, for the purposes of measuring small changes in air quality.

Their investigation into oxidative potential as a possible toxicologically relevant measure of exposure to the aggregate PM mixture was intriguing. However, their findings on the temporal and spatial changes in oxidative potential or in PM components related to the CCS were likely constrained by the same limitations that affected the first part of the study. The use of the oxidative potential assay in this study was largely exploratory, particularly with respect to its ability to discern the contributions of individual elements or classes of compounds in PM on archived filters. The HEI Health Review Committee thought the most interesting result was the modest suggestion that metals that have been associated with tire and brake wear might contribute to the oxidative activity levels observed. However, further work is necessary to solidify the role of oxidative potential in this assay, and in other assays of this nature, as an indicator of potential human toxicity.

Ultimately, the Review Committee concluded that the investigators, despite their considerable effort to study the impact of the London CCS, were unable to demonstrate a clear effect of the CCS either on individual air pollutant concentrations or on the oxidative potential of PM_{10}. The investigators' conclusion that the primary and exploratory analyses collectively indicate a weak effect of the CCS on air quality should be viewed cautiously. The results were not always consistent and the uncertainties surrounding them were not always clearly presented, making it difficult to reach definitive conclusions.

This study of the CCS in London adds to the growing body of evidence that confirms the need to establish the extent to which interventions have improved, or are likely to improve, ambient air quality before health studies are contemplated. These investigators, in essence, covered the first three steps in the "Outcomes Evaluation Cycle": they (1) provided evidence that the intervention or controls had in fact been put in place, (2) modeled the potential impact of the intervention on emissions, and (3) assessed whether the intervention had resulted in improved air quality. By choosing not to fund the evaluation of health outcomes that was originally proposed as part of the study, despite the projected reductions in emissions, HEI had emphasized the importance of meeting these initial requirements. The study's subsequent challenges in identifying an improvement in air quality reinforce that decision. Ultimately, although several factors affect the statistical power of studies to detect changes in health related to an intervention like the CCS, a documented expectation of a sufficient change in air quality is and will continue to be an important criterion for deciding whether to engage in a health outcomes study.

The Impact of the Congestion Charging Scheme on Air Quality in London
Part 1. Emissions Modeling and Analysis of Air Pollution Measurements

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ABSTRACT

On February 17, 2003, a congestion charging scheme (CCS*) was introduced in central London along with a program of traffic management measures. The scheme operated Monday through Friday, 7 AM to 6 PM. This program resulted in an 18% reduction in traffic volume and a 30% reduction in traffic congestion in the first year (2003). We developed methods to evaluate the possible effects of the scheme on air quality: We used a temporal–spatial design in which modeled and measured air quality data from roadside and background monitoring stations were used to compare time periods before (2001–2002) and after (2003–2004) the CCS was introduced and to compare the spatial area of the congestion charging zone (CCZ) with the rest of London.

In the first part of this project, we modeled changes in concentrations of oxides of nitrogen (NO_x), nitrogen dioxide (NO_2), and PM_{10} (particles with a mass median aerodynamic diameter $\leq$ 10 µm) across the CCZ and in Greater London under different traffic and emission scenarios for the periods before and after CCS introduction. Comparing model results within and outside the zone suggested that introducing the CCS would be associated with a net 0.8-µg/m^3 decrease in the mean concentration of PM_{10} and a net 1.7-ppb decrease in the mean concentration of NO_x within the CCZ. In contrast, a net 0.3-ppb increase in the mean concentration of NO_2 was predicted within the zone; this was partly explained by an expected increase in primary NO_2 emissions due to the introduction of particle traps on diesel buses (one part of the improvements in public transport associated with the CCS).

In the second part of the project, we established a CCS Study Database from measurements obtained from the London Air Quality Network (LAQN) for air pollution monitors sited to measure roadside and urban background concentrations. Fully ratified (validated) 15-minute mean carbon monoxide (CO), nitric oxide (NO), NO_2, NO_x, PM_{10}, and $PM_{2.5}$ data from each chosen monitoring site for the period from February 17, 2001, to February 16, 2005, were transferred from the LAQN database.

In the third part of our project, these data were used to compare geometric means for the 2 years before and the 2 years after the CCS was introduced. Temporal changes within the CCZ were compared with changes, over the same period, at similarly sited (roadside or background) monitors in a control area 8 km distant from the center of the CCZ. The analysis was confined to measurements obtained during the hours and days on which the scheme was in operation and focused on pollutants derived from vehicles (NO, NO_2, NO_x, PM_{10}, and CO).

This set of analyses was based on the limited data available from within the CCZ. When compared with data from outside the zone, we did not find evidence of temporal changes in roadside measurements of NO_x, NO, and NO_2, nor in urban background concentrations of NO_x. (The latter result, however, concealed divergent trends in NO, which fell, and NO_2, which rose.) Although based upon fewer stations, there was evidence that background concentrations of PM_{10} and CO fell within the CCZ compared with outside the zone.

This Investigators' Report is Part 1 of Health Effects Institute Research Report 155, which also includes *Part 2. Analysis of the Oxidative Potential of Particulate Matter*, a Commentary by the HEI Health Review Committee, and an HEI Statement about the research project. Correspondence concerning the Investigators' Report may be addressed to Professor Frank Kelly, Professor of Environmental Health, Environmental Research Group, MRC-HPA Centre for Environment & Health, School of Biomedical Sciences, King's College London, 150 Stamford Street, London SE1 9NH, U.K. Tel ++44 20 7848 4004; Fax ++44 20 7848 3891; frank.kelly@kcl.ac.uk.

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* A list of abbreviations and other terms appears at the end of the Investigators' Report.

We also analyzed the trends in background concentrations for all London monitoring stations; as distance from the center of the CCZ increased, we found some evidence of an increasing gradation in NO and PM_{10} concentrations before versus after the intervention. This suggests a possible intermediate effect on air quality in the area immediately surrounding the CCZ.

Although London is relatively well served with air quality monitoring stations, our study was restricted by the availability of only a few monitoring sites within the CCZ, and only one of those was at a roadside location. The results derived from this single roadside site are not likely to be an adequate basis for evaluating this complex urban traffic management scheme.

Our primary approach to assessing the impact of the CCS was to analyze the changes in geometric mean pollutant concentrations in the 2 years before and 2 years after the CCS was introduced and to compare changes at monitoring stations within the CCZ with those in a distant control area (8 km from the CCZ center) unlikely to be influenced by the CCS. We saw this as the most robust analytical approach with which to examine the CCS Study Database, but in the fourth part of the project we did consider three other approaches: ethane as an indicator of pollution dispersion; the cumulative sum (CUSUM) statistical technique; and bivariate polar plots for local emissions. All three were subsequently judged as requiring further development outside of the scope of this study. However, despite their investigative nature, each technique provided useful information supporting the main analyses.

The first method used ethane as a dispersion indicator to remove the inherent variability in air pollutant concentrations caused by changes in meteorology and atmospheric dispersion. The technique had the potential to ascertain more accurately the likely impacts of the CCS on London's air quality. Although this novel method appeared promising over short time periods, a number of concerns arose about whether the spatial and temporal variability of ethane over longer time periods would be representative of meteorologic conditions alone.

The major strength of CUSUM, the second method, is that it can be used to identify the approximate timing of changes that may have been caused by the CCS. This ability is weakened, however, by the effects of serial correlation (the correlation of data among measurements in successive time intervals) within air pollution data that is caused by seasonality and long-term meteorologic trends. The secure interpretation of CUSUM requires that the technique be adapted to take proper account of the underlying correlation between measurements without the use of smoothing functions that would obscure a stepped change in concentrations. Although CUSUM was not able to provide a quantitative estimation of changes in pollution levels arising from the introduction of the CCS, the strong signals that were identified were considered in the context of other results from the study.

The third method, bivariate polar plots, proved useful. The plots revealed important characteristics of the data from the only roadside monitoring site within the CCZ and highlighted the importance of considering prevailing weather conditions when positioning a roadside monitor. The technique would benefit from further development, however, in transforming the qualitative assessment of change into a quantitative assessment and including an estimate of uncertainty. Research is ongoing to develop this method in air-quality time-series studies.

Overall, using a range of measurement and modeling approaches, we found evidence of small changes in air quality after introduction of the CCS. These include small decreases in PM_{10}, NO, and CO. The possibility that some of these effects might reflect more general changes in London's air quality is suggested by the findings of somewhat similar changes in geometric means for weekends, when the CCS was not operating. However, since some evidence suggests that the CCS also had an impact on traffic volume on weekends, the CCS remains as one possible explanation for the observed pattern of changes in pollutant concentrations. In addition, the CCS was just one of a number of traffic and emission reduction schemes introduced in London over the 4-year study period; if the other measures had an impact in central London, they might partly explain our findings.

Although not the aim of this study, it is important to consider how the trends we observed might be translated

Air Monitoring Site Classifications in the London Air Quality Network

Rural. An open countryside location in an area of low population density distanced as far as possible from roads and populated and industrial areas.

Suburban. A location in a residential area on the outskirts of a town or city with no major sources of pollution within 50 m.

Urban Background (also referred to as background). An urban location with no major sources of pollution within 50 m and broadly representative of city-wide background conditions; for example, urban residential areas.

Roadside. A site sampling between 1 m from the curbside of a busy road and the back of the pavement (sidewalk). Typically this is within 5 m of the road, but could be up to 15 m.

Curbside. A site sampling within 1 m of the curb of a busy road.

into health effects. For example, given that London already has NO_2 concentrations in excess of the permitted limit value, we do not know what the effects of an increase in NO_2 created by diesel-exhaust after-treatment for particles might mean for health. Further, although it is not likely that NO affects health, the decrease in NO concentrations is likely associated with an increase in ozone concentrations (a pollutant associated with health effects), as has been seen in recent years in London. These and other similar issues require further investigation.

Although the CCS is a relatively simple traffic management scheme in the middle of a major urban environment, analyzing its possible impact on air quality was found to be far from straightforward. Using a range of modeling and monitoring approaches to address the impact of the scheme revealed that each technique has its own advantages and limitations. The placement of monitoring sites and the availably of traffic count data were also identified as key issues. The most compelling lesson we take away from this study is that such work is impossible to undertake without a coherent multi-disciplinary team of skilled researchers.

In conclusion, our study suggests that the introduction of the CCS in 2003 was associated with small temporal changes in air pollutant concentrations in central London compared with outer areas. However, attributing the cause of these changes to the CCS alone is not appropriate because the scheme was introduced at a time when other traffic and emissions interventions, which might have had a more concentrated effect in central London, were also being implemented.

INTRODUCTION

HISTORICAL BACKGROUND OF LONDON'S AIR QUALITY

Air pollution has been a serious problem in London since the 16th century owing to the city's importance as a commercial and industrial center and because of the high concentration of domestic coal burning. As a consequence, the city has long been referred to as "the big smoke" and has given its name to the combination of urban smoke and natural fog, namely "London smog." Concern over the health effects of London's poor air quality also dates back many centuries. In 1661 the diarist John Evelyn presented Charles II with a treatise on the problem, in which he suggested that smoke pollution would shorten the lives of Londoners (Evelyn 1661). Nearly 200 years later, an article in The Lancet (1856) stated that "The air of this great city is, as all know too well, polluted by a variety of noxious gases and vapors diffused or held in solution." The article went on to quote the Registrar-General at that time as saying "There can be no doubt that the dirty dust suspended in the air that the people of London breathe, often excites diseases of the respiratory organs. The dirt of the streets is produced and ground down by innumerable horses, omnibuses and carriages, and then beat up into fine dust, which fills the mouth, and inevitably enters the air passages in large quantities."

London's dominance as an industrial city and major port steadily declined during the 20th century, giving way to commerce and public administration as its major activities. Consequently, emissions of smoke and sulfur dioxide (SO_2) from industrial activities declined. Indeed, the annual mean black smoke concentrations fell by more than a factor of 80 over the period from 1922 to 1997 (Figure 1). In 1952, the infamous wintertime smog episode, which

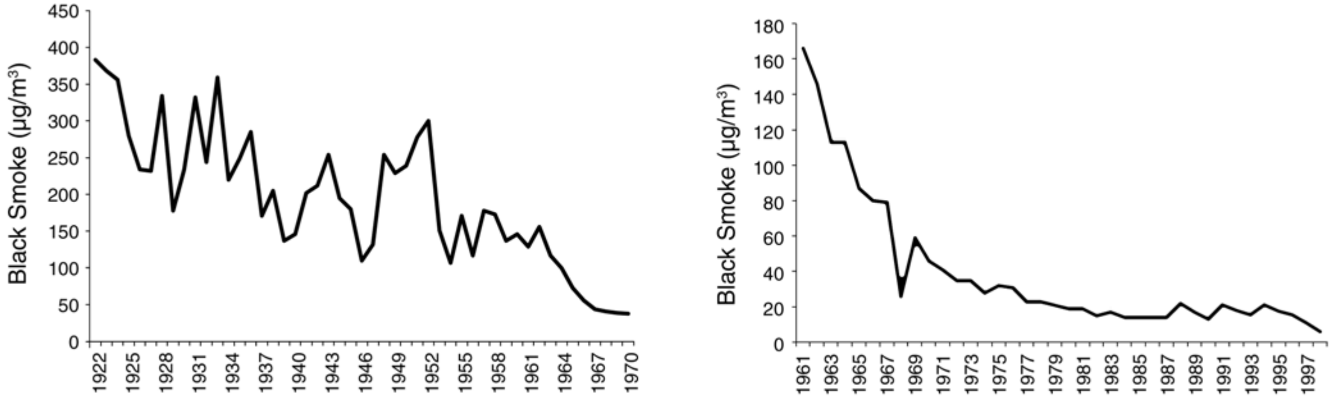


Figure 1. Historical black smoke concentrations in London. Left panel: data from the Kew Observatory from 1922 to 1969; right panel: data from the Lambeth air monitoring station from 1961 to 1998. Note that the units on the two *x* axes differ. Source: AQEG 2005.

claimed an estimated 4,000 to 12,000 premature deaths, had a major impact on public health policies and led to the 1956 Clean Air Act, the major focus of which was the curtailing of domestic coal burning in London and other major population centers in the United Kingdom. As Figure 1 shows, however, the 1956 Act reinforced the declining black smoke trends that were already well in hand due to structural changes in London's economy. Over the last 50 years coal burning has continued to decline, being replaced by centrally generated electricity and the use of natural gas in commercial premises and homes.

AIR POLLUTION IN LONDON TODAY

In December of 1991, a severe wintertime air pollution episode occurred in London. It was characterized by unprecedented levels of benzene, CO, NO_x, and in particular, NO_2 — all components of exhaust from gasoline- and diesel-powered motor vehicles. In response, new air quality monitoring sites were established in and around London and the equipment base of existing sites was extended. Continuous monitoring of PM_{10} began to replace the original black smoke measurements. In order to coordinate the air quality monitoring established by the 33 London Boroughs and to ensure spatial and temporal comparability, in 1993 the Environmental Research Group (ERG) at King's College London created the LAQN. The LAQN has generated a much clearer picture of London's air quality and the steps required to ensure its improvement. For example, analysis of the LAQN data shows that, during the 1990s and early 2000s, airborne particulate and lead concentrations have declined steadily after lead was phased out of gasoline, and levels of CO, benzene, and 1,3-butadiene have fallen dramatically (with annual reductions of 10% to 20%). Much of this improvement was brought about by the mandatory implementation of three-way catalysts and evaporative canisters in gasoline engines. In turn, the reduction in emissions of volatile organic compounds (VOCs) has produced a decline in the peak intensity of photochemical smog episodes.

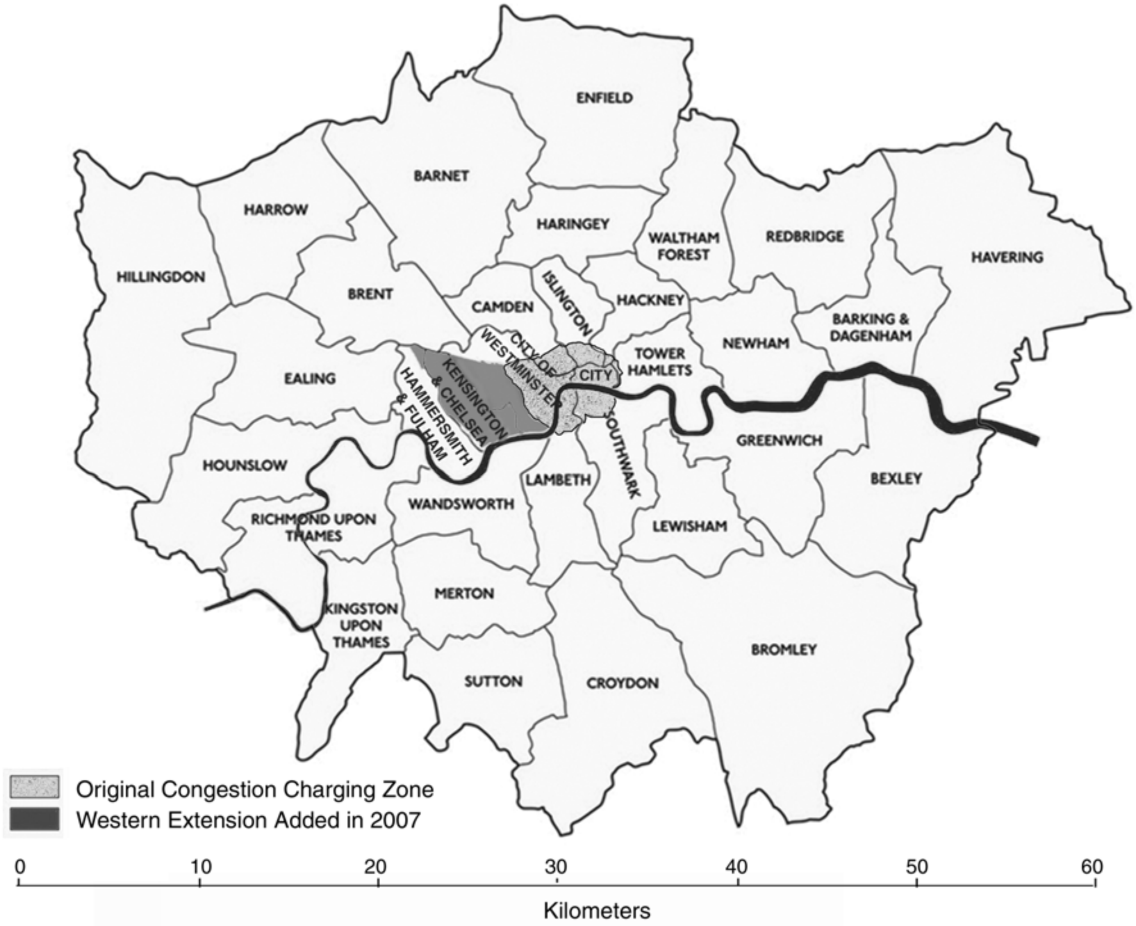


Figure 2. Relationship of the CCZ to Greater London. (Map includes the Western Extension, which was introduced in 2007.) Adapted with permission from Transport for London 2006.

In contrast, the annual percentage of reductions in NO_x levels (also achieved through use of three-way catalysts) of approximately 3% to 5% are substantially lower than those achieved for CO and VOCs. This is because of the substantial and growing contributions to NO_x emissions from diesel-powered motor vehicles which, until recently, had not been the target of emission controls. The increasing use of diesel-powered vehicles also means that PM is still of major concern despite the enormous reduction in black smoke levels. In fact, although concentrations of PM_{10} declined during the 1990s, the trend has slowed down and, during the early 2000s, levels have remained constant. So despite the air quality gains achieved in previous decades, like many other large cities around the world, London continues to have high levels of air pollution owing to a combination of mobile and regional background sources.

LONDON'S AIR QUALITY STRATEGY

In view of widespread public concern about the health effects of air pollution, in 2002 the Mayor of London launched his Air Quality Strategy, entitled Cleaning London's Air (Greater London Authority 2002). It set out policies and proposals to move toward the point where pollution no longer poses a significant risk to human health. The primary focus of the strategy was the reduction of pollution from road traffic in the city since this is the main source of the pollutants of concern. In 2003, emissions from road transport contributed approximately 40% of NO_x emissions and 66% of PM_{10} emissions in Inner London. A reduction in London's road traffic emissions is being achieved through two goals: decrease the number of vehicles on the road, and reduce emissions from individual vehicles (i.e., modernize the vehicle stock). To help achieve the first goal, the Mayor introduced a CCS in central London on February 17, 2003. One approach to tackle the second goal is a London-wide Low Emission Zone, which was introduced on February 4, 2008 (see Kelly et al. 2011).

THE CCS IN LONDON

The CCS is a scheme to charge vehicles that enter a specific zone. It initially covered approximately 22 km^2 or 1.4% of the Greater London area (enclosed approximately by the M25 London Orbital Motorway [Figure 2]) and contained some of the most congested traffic conditions in London. On February 19, 2007, the CCZ was extended westward to cover approximately 41.5 km^2 or 2.6% of the Greater London area (Figure 3). The designated zone is clearly defined by signs or road markings at entrance and

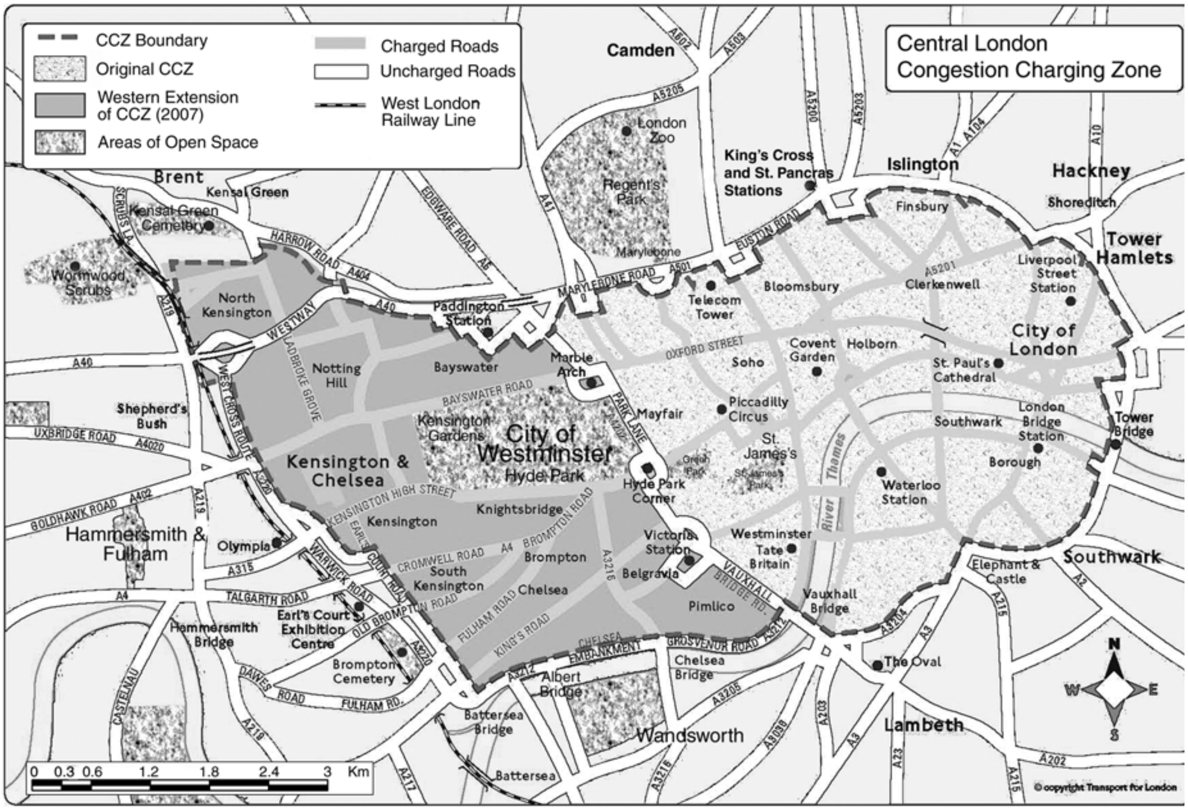


Figure 3. The CCZ with the 2007 Western Extension (in gray). The middle road that separates the original zone and the Western Extension is uncharged. Adapted with permission from Transport for London 2006.

exit points. Vehicles that cross a cordon line on weekdays between 7:00 AM and 6:00 PM, referred to as the congestion charging hours (CCH), pay a daily charge that was originally 5 Great Britain pounds (then about 8 U.S. dollars) but was increased to 8 GBP (then about 14 USD) in July 2005. The charge does not apply on national holidays or the first 3 charging days that follow December 26 each year. Vehicles that are exempt from the charge include those for individuals with disabilities and institutions that assist them throughout the European Union (which are identified by blue badges), roadside recovery vehicles (towing trucks), accredited roadside breakdown organizations, electrically propelled vehicles, vehicles with nine or more seats and registered as buses, licensed taxis, and motor tricycles 1 m or less in width and 2 m or less in length. In addition to these exemptions, discounts are available to residents living within the CCZ (90% reduction in fee) and drivers of vehicles powered by alternative fuels (up to 100% reduction). Assisted by revenue from the CCS, concurrent improvements in traffic management and in the fleet of public transport vehicles have been implemented to accommodate the shift in travel patterns after the introduction of the CCS as well as continued growth in passenger numbers.

The main objective of the CCS was to achieve a 15% reduction in traffic in the CCZ and 0% growth in traffic in Inner London surrounding the CCZ; each year, the principal traffic and transport objectives have been met. This success mirrors the effectiveness of similar schemes in Singapore, Stockholm, and Norway (Chin 1996; Tuan Seik 2000; Victoria Policy Transport Institute 2007). Changes to travel patterns (e.g., traffic entering the CCZ, congestion, and speeds) that have arisen from the scheme occurred very quickly in 2003; however, changes in the period since have tended to reflect wider traffic trends and possibly effects that have developed more slowly from the CCS and other transport changes. These immediate and longer-term effects are discussed below.

At the end of the first year of CCS operation, the number of vehicles with four or more wheels that entered the zone during charging hours had dropped by 18% from 2002 numbers; the most recent results reported from Transport for London (TfL; the local government body responsible for managing the London transport system) illustrate that such a reduction continues: traffic entering the CCZ during 2006 was 21% lower than the pre-CCS conditions in 2002 (TfL 2007). In contrast to findings within the CCZ, traffic on the Inner Ring Road (IRR; the boundary of the CCZ along which no charge is applied) has remained similar to levels before charging was introduced. As one would expect, the immediate effect 1 year after the start of the CCS was that the number of chargeable vehicles (i.e., cars, minicabs [privately hired vehicles, limousines], vans [delivery vehicles], and lorries [trucks]) entering the CCZ during charging hours was lower; at the same time, the number of non-chargeable vehicles such as licensed taxis, buses, and two-wheelers all increased (Tfl 2007). In comparing values for 2006 against those for 2003, we saw further declines across most vehicle types.

Evaluating the overall impact of the CCS on congestion is more complex. (Congestion is defined as excess delay [minutes/km] over and above uncongested conditions, which are the early hours of the morning [1–5 AM].) During 2003 and 2004, levels of congestion in the CCZ were typically around 30% lower than those in 2002; but in 2005 the average congestion reduction was only 22%. Moreover, during 2006, despite a continued reduction in vehicle count, congestion increased to higher than the 2002 levels. This change correlated with an increase in road work and with a gradual longer-term trend of increased congestion across London.

In line with the decrease in vehicle counts, the introduction of the CCS substantially increased traffic speeds during charging hours from 14 km/hour in 2002 to approximately 17 km/hour in 2003 (a level last seen in the early 1980s). Since 2003 however, average speeds observed during charging hours have progressively fallen back to about 16 km/hour in 2005 and 15 km/hour in 2006 (TfL 2007).

Similar road pricing schemes are being considered for other U.K. cities and it is likely that traffic zone payment schemes will become more common elsewhere in the world. For example, Milan tested such a scheme at the beginning of 2007 to address the city's severe air pollution and traffic problems; and New York City is the first major American city to seriously consider implementing a traffic congestion charge. The CCS in London can thus be considered a forerunner in what is likely to become a powerful and widely adopted approach to traffic management.

THE CCS AND AIR QUALITY IN LONDON

In the current HEI study, we assessed whether the reduction in congestion and traffic achieved after a regulatory intervention has had an impact on the air quality in London. In principle, by reducing the number of vehicles entering the zone, the CCS should reduce emissions and improve air quality in the center of London. However, this is an unrealistically simple assumption. We did not expect the CCS to have more than a small effect on air quality within the CCZ considering that it brought about a relatively moderate reduction in traffic (approximately 20% fewer vehicles) in a small area (1.4%) of Greater London.

A number of other factors made it likely that the effect elicited would be small. First, changes brought about by the CCS could have competing impacts on air quality. For example, traffic flow and vehicle speed have the potential to produce both increases and decreases in PM and NO_x emissions. Improvements in public transport vehicles (e.g., retrofitting diesel engines with catalytic converters) can be offset by an increase in the number and distribution of diesel-powered buses and taxis entering the CCZ. The introduction of other traffic management measures and the magnitude and location of road improvement worksites could all have an impact.

London air quality may also be affected by broader temporal trends in traffic and other sources of emissions. For example, the apparent gradual trend of increased congestion across London over time could obscure the small changes in air quality in the short term. A host of other pollutant contributors in London, regional background sources, and more distant sources such as continental Europe, coupled with annual meteorologic variations could all confuse air pollution trends.

Whether the CCS results are observable depends also on the number and location of air quality monitors. Unfortunately, our study was compromised by an insufficient number of monitoring stations at optimal locations; in particular, too few sites were available within the CCZ and only one of those was positioned at a roadside, where the impact would likely be greatest.

Using the methods detailed below, we have, whenever within our control, addressed these many issues and in doing so, taken a multi-faceted approach to assess the impact of the CCS on London's air quality.

Our research began with a detailed exercise in comparative emissions modeling. A previous modeling assessment had been undertaken (Beevers and Carslaw 2005) based on the 2002 London Atmospheric Emissions Inventory (LAEI; a database of air pollutant emissions from all roadway and non-roadway sources). The work conducted as part of this project used the 2003 LAEI data, which became available in 2006. With these updated estimates of emissions across London, we modeled the impact of the CCS on air quality in a manner that would provide a comparator for the outcomes of subsequent analysis of air quality measurements made before and after introduction of the CCS.

The next activity involved assembling an air pollution database — the CCS Study Database — that would be used to investigate changes in air quality associated with the introduction of the CCS. This database contained ratified data from 102 monitoring sites across Greater London. To analyze the impact of the CCS on air quality, a number of key indicator sites were identified. These sites were located in three areas: within the CCZ, in Inner London (i.e., the area surrounding the CCZ), and a representative sample of control sites from suburban areas in Outer London.

We then considered four analytical techniques for the analysis of the CCS Study Database. In the first, changes in mean pollutant concentrations before and after the CCS was introduced were compared with changes at monitoring stations unlikely to have been influenced by the CCS. The three remaining techniques were tested: (a) ethane, which emanates at a constant rate from leaking gas pipes, was used to adjust pollutant measurements for dispersion due to meteorologic and atmospheric factors; (b) the CUSUM statistical technique was used to identify a change point in the trends in air pollution concentration over time; and (c) bivariate polar plot analysis was used to identify the portion of the pollutant dataset that could be directly related to emissions from the roads adjacent to a particular monitoring site. These later three approaches were ultimately judged as requiring further development outside the scope of the study.

SPECIFIC AIMS

The overall objective of the current study was to assess whether the reduction in traffic congestion in London (achieved by the introduction of the CCS covering 1.4% of the Greater London area, which contains some of the most congested traffic conditions in the city) has had an impact on air quality in London. The research undertaken on this environmental initiative has allowed us to progress part way along the "chain of accountability," the series of steps that begins with implementing an air quality intervention and leads to determining whether it has had the desired effect on emissions, on air quality, and ultimately on human health (HEI Accountability Working Group 2003; and as described in the Preface to this Research Report). The outcome of this research has the potential to provide an analytical framework for and to help inform future decisions about similar road pricing schemes that may gradually be introduced in other cities around the world. To achieve our overall objective the following specific aims were agreed upon.

1. To update and verify the tools needed to undertake detailed comparative emission scenarios and concentration modeling for the CCZ and surrounding areas. To then undertake a detailed modeling exercise to examine the impact of the CCS.
2. To assemble a CCS Study Database from monitoring sites in Greater London to assess the impact of the CCS.
3. To examine a range of analytical approaches to investigate the emissions and monitoring data.

4. To examine the oxidative potential of PM collected on filters before and after the CCS was introduced (described in Part 2 of this Research Report).

MODELING THE AIR POLLUTION IMPACTS OF THE CCS IN LONDON

INTRODUCTION

Before the start of this project, an assessment of the possible impact of the CCS on air pollution emissions predicted a reduction of 12% for NO_x and 11.9% for PM_{10} (Beevers and Carslaw 2005). These preliminary projections were calculated using the LAEI 2002 data. The LAEI area covers the road network up to and including the M25 Motorway and includes information on traffic flow and vehicle speed.

Since that initial analysis, the LAEI 2002 data have been superseded by the LAEI 2003 data (Mattai and Hutchinson 2006). The current analyses of emissions and air pollution concentrations were based on a combination of the LAEI 2003 data, and, for all non-traffic emissions, the King's College London Emissions Toolkit (LET) and the King's College London Air Pollution Toolkit (LAPT). For more detailed descriptions of these tools see Appendices D and E (available on the HEI Web site). Comprehensive counts of traffic entering and leaving the CCZ across road-based entry and exit points were conducted twice yearly by TfL. These combined counts were used to produce an annual estimate of traffic volume for each year considered in this study.

METHODS

The King's College LET for Road Traffic

The LET, a set of databases with vehicle stock and age profiles, emission factors, and emission models, was used to predict detailed traffic emissions for 6344 roads and for these vehicle types: cars, motorcycles, taxis, light-goods vehicles (LGVs), buses (London Transport [LT] and non-LT), and rigid and articulated heavy-goods vehicles (HGVs). Emissions included NO_x, NO_2, PM_{10} from exhaust, PM_{10} from tire and brake wear, and carbon dioxide (CO_2) under different traffic scenarios for the periods before and after the CCS was introduced. PM_{10} resuspension was not included because of the uncertainty associated with emission factors for this source and because recent studies have found it to contribute a very small proportion of primary PM_{10} emissions in London (Harrison et al. 2004).

The LET is used to simulate exhaust emissions from the road traffic flows and speeds (which are expressed as annual average daily traffic [AADT] values) for each of the individual roadway lengths or links in the entire London road network (the simulation method is described in detail in Appendix D, available on the HEI Web site). Calculating emissions from flows and speeds requires knowledge or assumptions about the mix of vehicles, their ages, and the emission standards with which each vehicle is intended to comply. The proportions of different vehicle types, classified by the European Union emission standards (e.g., Pre-Euro, Euro 1, Euro 2) are based on data provided by the Department for Transport. For buses and taxis, the model relies on London-specific data on the age and composition of the vehicle fleet. Given these assumptions about the fleet's composition, exhaust emissions in grams per kilometer per second are calculated using emission curves specific to each vehicle class (e.g., for a car, bus, or taxi meeting Euro 2 standards; described by Barlow and colleagues [2001]). Emissions from tire and brake wear are estimated in a similar manner but using different standard curves (Ntziachristos and Boulter 2003). Total annual emissions for each pollutant are estimated by aggregating emissions from all individual roadway lengths across the London network and presented in tonnes per year.

A number of assumptions were used to simulate the installation of exhaust after-treatment devices. For example, fitting particle traps to large diesel vehicles was assumed to reduce emissions of NO_x by 5% and of PM_{10} by 95%, and to increase CO_2 emissions by 0.8%; fitting selective catalytic reduction devices to large diesel vehicles was assumed to reduce emissions of NO_x by 50%. Exhaust emissions from vehicles with hydrogen fuel cells were assumed to be zero, but PM_{10} tire- and brake-wear emissions were assumed to be the same as for other vehicles.

The King's College LAPT

With the LAPT, a set of dispersion models and data sets, we predicted annual mean ambient concentrations of NO_x, NO_2, and PM_{10} from both vehicular and non-vehicular sources. The LAPT is capable of modeling more than one million individual sources with different source characteristics and has a typical output grid resolution of 20 × 20 m. Data for emission sources other than road transport were taken from the LAEI 2003 and included the following: Part A processes (large regulated industrial processes), Part B processes (smaller regulated industrial processes), boilers (large boiler plants), gas/oil/coal (domestic and commercial combustion), agriculture and nature, rail, ships, and airports.

RESULTS

LAPT Model Predictions of Air Pollutant Concentrations for 2001 Through 2004

To test the reliability of the LAPT, we used it to predict annual mean concentrations for NO_x, NO_2, and PM_{10} for each of the years from 2001 through 2004. (A comparison of the model's predictions with actual measurement data collected into the CCS Study Database is described in Appendix F, available on the HEI Web site.) In summary, the LAPT predicted the concentrations at most measurement sites to within ± 30% of measured concentrations and did not exhibit significant bias in the results. We concluded that the LAPT model provided a reasonable prediction of the spatial variability of the three pollutants across London for each of the years considered.

LET Model Predictions of Vehicle Emission Concentrations for 2001 Through 2004

We calculated detailed emission estimates for all major sources in London for the following pollutants: NO_x, NO_2, PM_{10}, and CO_2. PM_{10} was further broken down into its constituent components of PM_{10} from exhaust and PM_{10} from tire and brake wear. The road traffic sources were subdivided into total emissions by location in London, which included: within the CCZ, Inner London, Outer London, and External London (outside Greater London and up to the M25 London Orbital Motorway). Figure 4 is a map of these areas.

The predicted emissions demonstrate the relative importance of each zone and each pollutant. This is important because the CCZ itself is quite small — only 1.4% of the Greater London area. In the proportion of emissions,

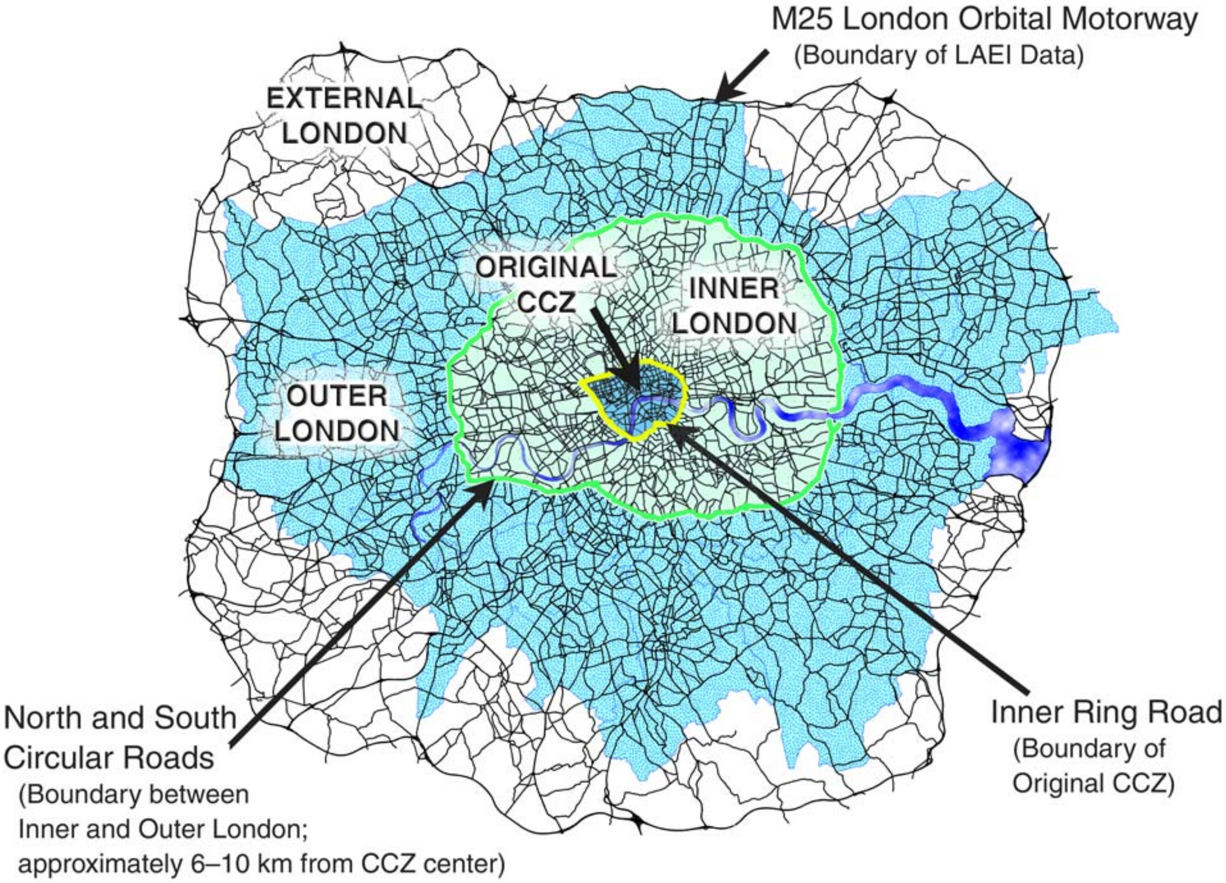


Figure 4. Areas of London. The Inner Ring Road bounds the original CCZ; the North and South Circular Roads are the outer border of Inner London; the remainder of the shaded area is Outer London; and the unshaded areas between Outer London and the M25 London Orbital Motorway are External London. Greater London encompasses the entire shaded area (the CCZ through Outer London). The M25 also encloses the area covered by the LAEI database.

Table 1. Non-Vehicle Emissions in London[a]

	2001			2002			2003			2004		
	NO_x	PM_{10}	CO_2	NO_x	PM_{10}	CO_2	NO_x	PM_{10}	CO_2	NO_x	PM_{10}	CO_2
Combustion												
Domestic gas	15,533	112	11,700,480	15,533	112	11,700,480	15,533	112	11,700,480	15,603	113	11,753,847
Domestic oil	83	2	104,988	83	2	104,988	70	2	104,988	70	2	104,988
Commercial gas	13,985	307	5,826,350	13,985	307	5,826,350	13,985	307	5,826,350	14,073	309	5,863,152
Commercial oil	216	17	268,183	216	17	268,183	216	17	268,183	216	17	268,183
Small industrial processes	510	271	55,889	510	271	55,889	336	271	55,889	336	271	55,889
Ships	196	2	9,403	196	2	9,403	183	2	9,403	183	2	9,590
Railways	3,813	143	221,449	3,813	143	221,449	3,702	138	221,449	3,635	129	218,423
Large industrial processes	5,652	49	8,180,472	5,652	49	8,180,472	5,652	49	8,180,472	5,652	49	8,180,472
Aircraft	2,248	109	1,154,862	2,248	109	1,154,862	2,248	109	1,154,862	2,258	110	1,176,133

[a] All emissions are totals calculated from the LAEI 2003 data up to and including the M25 Motorway. Source categories that were not included do not contribute significantly to London emissions. The precision with which the emissions are reported is not meant to reflect the accuracy of the estimate. In addition, no formal uncertainty estimate of these emissions has been undertaken for the LAEI 2003 data. Values are shown in metric tonnes (1000 kg or ~2205 pounds) per year.

the CCZ is also relatively small; for example, in 2002 the CCZ represented 4.2% of total road traffic NO_x emissions; for NO_2 it was 4.8%; and for CO_2 it was 4.0%. For PM_{10} emissions a similar picture emerged in that the CCZ represented 4.9% of the total PM_{10} from both exhaust and tire and brake wear, 5.7% of total PM_{10} from exhaust, and 3.3% of total PM_{10} from tire and brake wear. The CCZ did, however, have the highest NO_2-to-NO_x emissions ratio (15%) of any area of London.

It is important to consider the relative contribution that road traffic emissions would make toward total London emissions. Summarized in Table 1 are estimated emissions from the major non-vehicle sources of NO_x, PM_{10}, and CO_2 in London. These emissions represent the totals for each category across the whole LAEI area (out to the M25 Motorway). In 2002, for the whole LAEI, road traffic represented 55% of total NO_x emissions, 77% of PM_{10} emissions, and 30% of CO_2 emissions.

Emission Assumptions for the Air Pollution Model

The limited number of years covered by the LAEI 2003 database required that a number of assumptions be made to model air pollutant levels for the 2 years before and after CCS implementation in 2003. The LAEI 2003 database summarizes emissions from non-vehicle sources for only 2 years — 2003 and 2010. Review of those emissions data for London suggested that the changes over time in non-vehicle emissions are very small compared with changes in vehicle-related emissions; therefore, we assumed that emissions from most of the non-vehicle sources in 2001 and 2002 would be constant at the 2003 levels even though small changes would occur for some of these sources (for example, those of ships, railways, small industrial processes, and domestic oil). For 2004, a more comprehensive data set of emission changes was made possible by interpolating between LAEI predictions for 2003 and 2010, although they were still small in magnitude.

In contrast, the gradual change in vehicle technology would be expected to lead to improvements in emissions between 2001 and 2004. The emission estimates for each year were created using detailed changes in vehicle stock (summarized into European Union emission class categories), changes in vehicle-kilometers traveled (VKT), and changes in vehicle speed estimated for each road link. The most important of these changes was vehicle stock; for each of the 4 years, details for the following vehicle types were used: cars, motorcycles, taxis, light-goods vehicles, LT and non-LT buses, and rigid and articulated heavy-goods vehicles.

For all but LT buses and taxis, the estimates of vehicle stock were made using the U.K. National Stock model (T. Murrells, personal communication, August, 2005); for the remaining two vehicle categories, stock details were provided by London Transport Buses (A. Rickard, personal communication, August, 2005) and the Greater London Authority (S. Legge, personal communication, August, 2005). Changes in VKT between years were small; however, changes were applied across London using estimates provided by TfL (C. Buckingham, personal communication, August, 2005). The exceptions were the changes in VKT associated with the CCZ and IRR between 2002 and 2003. For these groups of roads, changes were made using the published statistics from TfL (2004). Finally, vehicle speed estimates were updated each year using average link speed data from the "floating car," a continuously circulating vehicle in London.

These calculations estimated that London's total emissions of NO_x would decrease by 26% from 57,751 tonnes/ year in 2001 to 42,613 tonnes/year in 2004 (a tonne is 1000 kg or ~ 2205 pounds; Table 2). Over the same period, NO_2 emissions were predicted to drop only 6% from 6888 tonnes/year to 6454 tonnes/year; hence, the NO_2-to-NO_x emissions ratio was predicted to increase from 11.9% to 15.1%. The emissions reductions of CO_2 over the same period were predicted to be only 2.6%. Over the same period, PM_{10} total vehicular emissions (PM exhaust and tire and brake wear) were predicted to drop from 3602 tonnes/year to 2861 tonnes/year, a decrease of 21% (Table 3). Although PM_{10} emissions from exhaust were predicted to decrease by 29%, tire- and brake-wear emissions were predicted not to change; hence the modeled contribution to total vehicle PM_{10} emissions from tire and brake wear increased from 29% to 36%. If this is a true reflection of ambient emissions, it has important policy implications for controlling PM_{10}: the focus should not be exclusively on reductions of tailpipe emissions.

Air Pollution Predictions for 2001 Through 2004

Concentrations of NO_x, NO_2, and PM_{10} were predicted for 2001 through 2004 and annual means across Greater London were calculated. Figures 5, 6, and 7 show the contributions of different sources of air pollution to the total in Greater London. The visibility of the major roads clearly

Table 2. Predicted Vehicle Emissions of NO_x, NO_2, and CO_2 for 2001 Through 2004[a]

Location	2001	2002	2003	2004
NO_x				
Within CCZ	1,456	1,363	1,174	1,090
Inner London	10,943	9,966	8,956	8,313
Outer London	23,987	21,487	19,185	17,564
External London	21,365	19,081	17,153	15,646
Total London	57,751	51,897	46,468	42,613
NO_2				
Within CCZ	207	206	195	199
Inner London	1,395	1,371	1,332	1,357
Outer London	2,824	2,754	2,673	2,692
External London	2,462	2,349	2,257	2,206
Total London	6,888	6,680	6,458	6,454
NO_2/NO_x (%)				
Within CCZ	14.2	15.1	16.6	18.3
Inner London	12.8	13.8	14.9	16.3
Outer London	11.8	12.8	13.9	15.3
External London	11.5	12.3	13.2	14.1
Total London	11.9	12.9	13.9	15.1
CO_2				
Within CCZ	323,676	319,635	265,253	256,391
Inner London	2,516,322	2,488,935	2,442,968	2,405,972
Outer London	5,247,442	5,206,320	5,196,065	5,130,339
External London	3,785,818	3,778,272	3,797,223	3,772,310
Total London	11,873,259	11,793,162	11,701,509	11,565,012

[a] The precision with which the emissions are reported is not meant to reflect the accuracy of the estimate. We estimated that NO_x emission totals had an uncertainty of ± 24% (2 SD). See Appendix D (available on the HEI Web site). Values are shown in metric tonnes (1000 kg or ~2205 pounds) per year.

Table 3. Predicted Vehicle Emissions of PM_{10} for 2001 Through 2004[a]

Location	2001	2002	2003	2004
Total PM_{10}				
Within CCZ	128	118	99	90
Inner London	871	806	725	673
Outer London	1623	1506	1390	1298
External London	981	914	854	800
Total London	3602	3344	3068	2861
Exhaust PM_{10}				
Within CCZ	102	93	76	68
Inner London	624	559	479	429
Outer London	1110	994	873	785
External London	730	663	600	548
Total London	2567	2309	2028	1828
Tire- & brake-wear PM_{10}				
Within CCZ	26	26	23	23
Inner London	247	247	246	244
Outer London	512	512	517	513
External London	251	251	254	252
Total London	1036	1036	1040	1032

[a] The precision with which the emissions are reported is not meant to reflect the accuracy of the estimate. We estimated that PM_{10} exhaust emission totals had an uncertainty of ±22% (2 SD) and that tire- and brake-wear PM_{10} emission totals had an order of magnitude uncertainty. See Appendix D (available on the HEI Web site). Values are shown in metric tonnes (1000 kg or ~2205 pounds) per year.

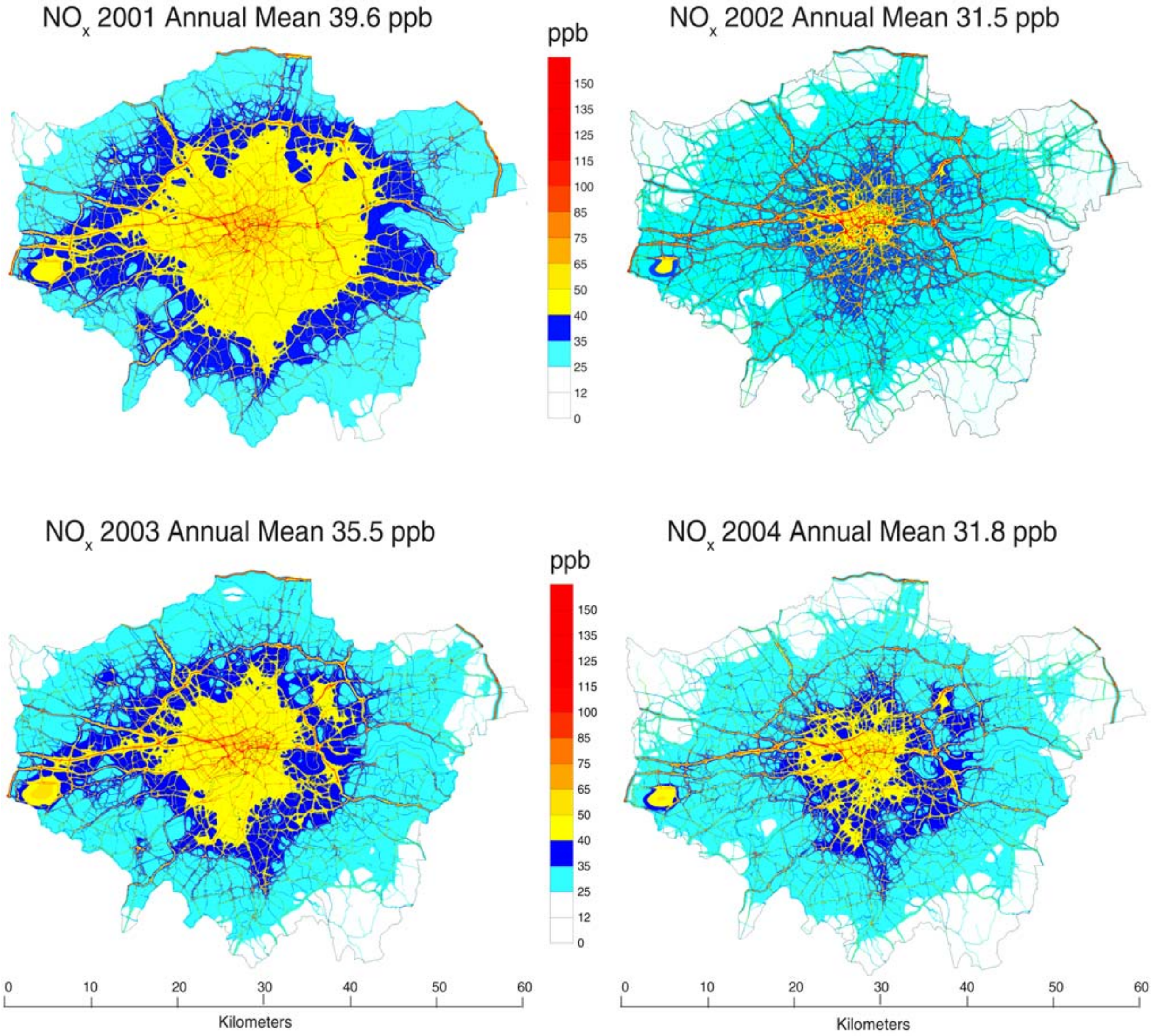
shows that road traffic contributes substantially to all three pollutants, but is especially important for NO_x (Figure 5) and NO_2 (Figure 6). It is also evident that toward the center of London a combination of sources, including vehicle emissions and gas combustion, resulted in the highest concentrations in the Greater London area. Other sources also contributed significantly to the pollution burden: the Heathrow Airport at the western fringe of London and the railway line running from Paddington in central London toward and past Heathrow. Finally, on the perimeter of External London, contributions can be seen from the M25 London Orbital Motorway.

The differences in predicted concentrations for the outer edges of Greater London and for the center of London also provide a good indication of the "London increment" of air pollution — the difference between concentrations in Greater London and those in the rural area surrounding it. Again, NO_x and NO_2 show the largest ranges of concentrations. The model results also showed that concentrations can vary widely (for example, the comparison between mean NO_x and NO_2 in 2001 [39.6 ppb and 21.4 ppb, respectively] and 2002 [31.5 ppb and 18.9 ppb, respectively]). A comparison between the NO_2 predictions displayed in Figure 6 and the World Health Organization (WHO) annual mean standard of 21 ppb (Air Quality Guidelines 2005) also suggests that the standard was likely to have been exceeded in large areas of London for all 4 years, but that the sizes of these areas were likely to vary widely year by year.

Predicted PM_{10} concentrations (Figure 7) across London look similar to those of NO_x (Figure 5) and NO_2 (Figure 6) in that road traffic is an important contributor. However, some important differences relate specifically to the range of concentrations across London and the size of the London increment. Specifically, the PM_{10} concentration in Greater London was predicted to be much smaller than that for NO_x and, as a consequence, the year-by-year variation in PM_{10} was predicted to be more closely associated with the contribution from outside Greater London. This was likely to have been particularly important during 2003 when a number of PM_{10} episodes occurred that contained significant proportions of secondary aerosol, which is associated with long-range transport of pollutants (Fuller 2005).

Comparison of Projected Air Pollutant Concentrations Before and After CCS Introduction for Within and Outside the Zone

NO_x, NO_2, and PM_{10} concentrations have been summarized into periods before (2001 and 2002) and after (2003 and 2004) the CCS was implemented as well as into average concentrations within and outside the zone. (For this analysis, "outside" includes both Inner and Outer London; see Figure 4.) The comparisons of the predicted


NO_x 2001 Annual Mean 39.6 ppb

NO_x 2002 Annual Mean 31.5 ppb

NO_x 2003 Annual Mean 35.5 ppb

NO_x 2004 Annual Mean 31.8 ppb

Figure 5. Modeled NO_x concentrations (ppb) for 2001, 2002, 2003, and 2004. Each projected annual mean is the average of approximately 4.4 million 20- × 20-m predictions for Greater London.

concentrations from the before-and-after models were also summarized into difference plots (post CCS − pre CCS) for NO_x and NO_2 (in ppb) and PM_{10} (in µg/m^3; see Figures 8, 9, and 10). The methods adopted to create the difference plots were intended to be comparable to the analysis of the air pollution measurements described later (see the section Analysis of Temporal Changes in Mean Measured Pollutant Concentrations Across London); in other words, we compared changes before and after the CCS implementation within the CCZ with those outside the zone beyond the influence of the CCS.

The analytic approaches to characterizing the changes in the *modeled* and *measured* concentrations, however, differed in some important ways.

- First, the model predicted annual arithmetic mean concentrations for 7 full days in each week; the measured concentrations were analyzed as geometric means for scheme hours only (7:00 AM to 6:00 PM).
- Second, the model defined "outside the zone" as including both Inner and Outer London; the analysis of measured concentrations used a control area that

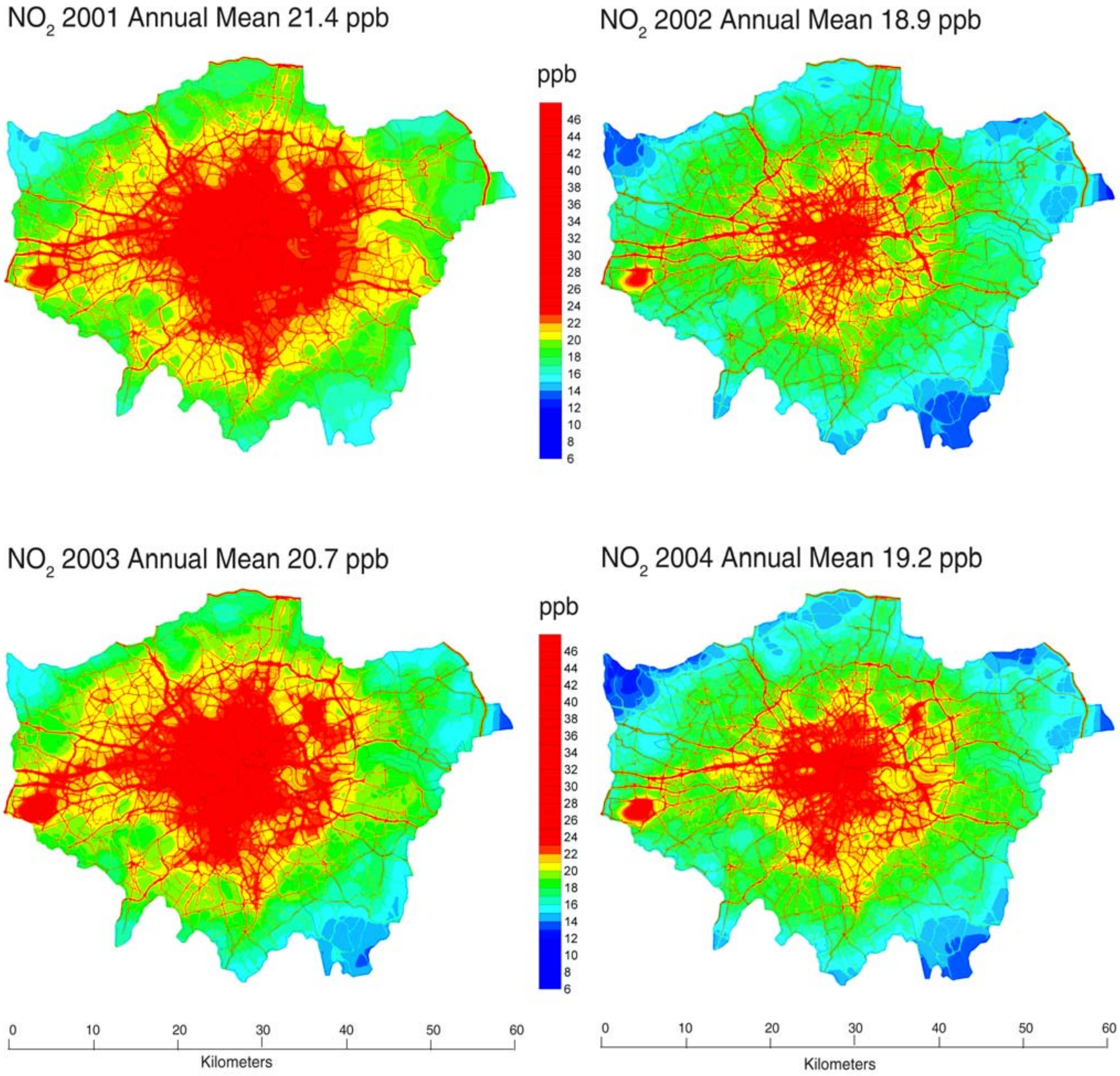


Figure 6. Modeled NO_2 concentrations (ppb) for 2001, 2002, 2003, and 2004. Each projected annual mean is the average of approximately 4.4 million 20- × 20-m predictions for Greater London.

started 8 km from the center of the CCZ and extended to the boundary of Greater London (see Figure 16 in a later section).

- Third, the modeling studies estimated changes in pollutant concentrations averaged over each area (within and outside the zone); the measurement studies calculated differences in air quality at individual monitoring sites where changes may be more localized.

In addition, because the model results were averaged across large areas, they were dominated by contributions from regional background concentrations; they are thus more likely to resemble measurement results obtained at background, rather than roadside, monitoring sites.

The estimated changes in concentrations from before to after CCS implementation were small (e.g., 1.9 ppb NO_X) in relation to the uncertainties in concentrations predicted

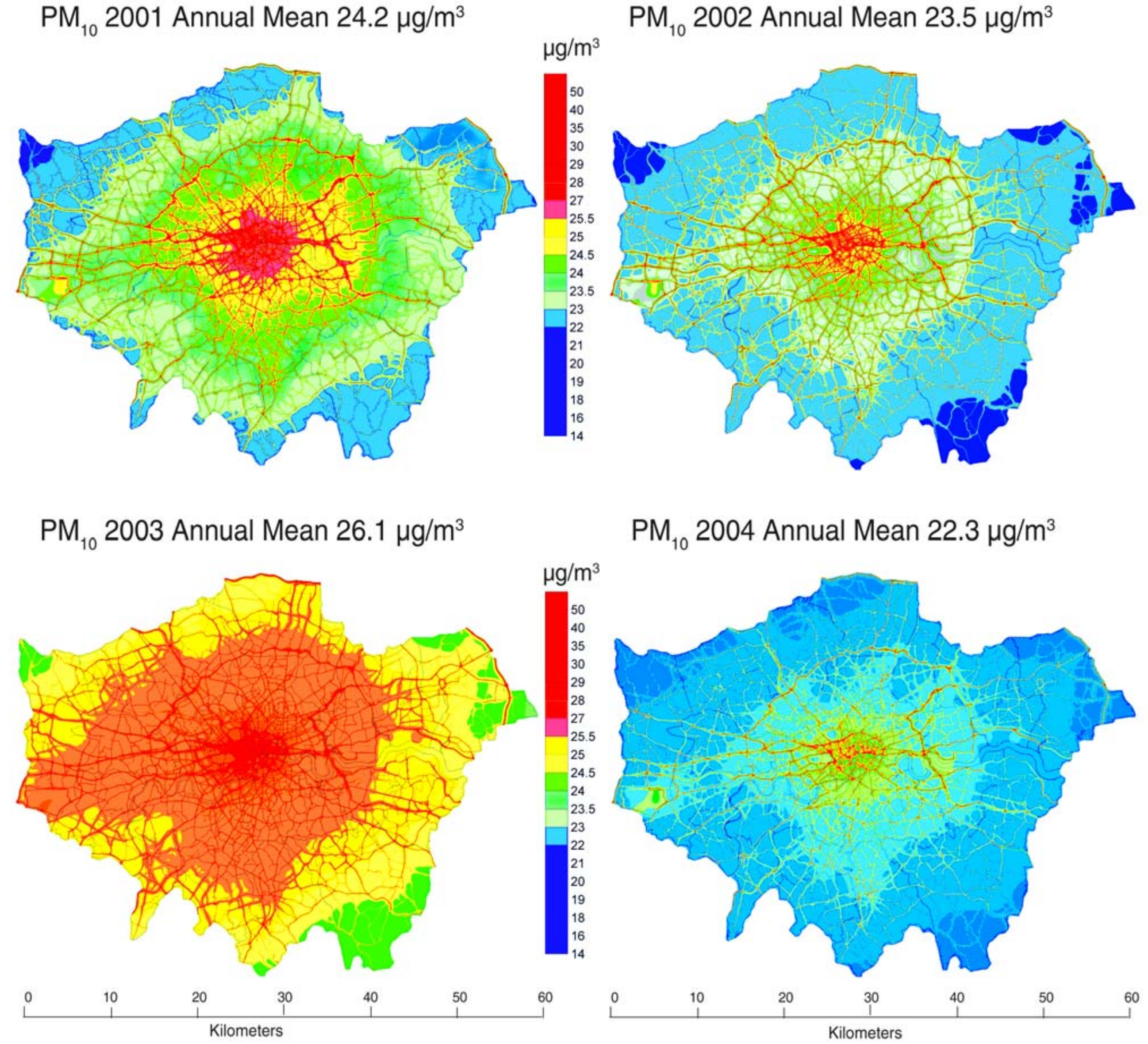


Figure 7. Modeled PM_{10} concentrations (µg/m^3) for 2001, 2002, 2003, and 2004. Each projected annual mean is the average of approximately 4.4 million 20- × 20-m predictions for Greater London.

from the model (see Appendix Table F.1, which gives an average root mean squared [RMS)] error of 14.4 ppb.

Some further context for the estimated changes in area-wide mean concentrations of individual pollutants in relation to spatial variation (as indicated by standard deviations) across areas is provided in Table 4. The table suggests that spatial variation is expected to be much larger than the differences in mean pollutant concentrations estimated for the periods before and after CCS implementation.

The difference map of Greater London for NO_x (Figure 8) shows that the air pollution model predicted that NO_x concentrations would drop between pre- and post-CCS periods and that this reduction would be greater moving from west to east. This pattern could reflect a combination of prevailing westerly winds, changes in VKT, and that vehicle emission reductions during 2001 to 2004 might have had more influence toward the east of London. However further investigation would be required to confirm this.

In contrast, the models suggested that areas with emission sources whose activities either decreased very little (railways) or increased (Heathrow Airport) during this time were likely to experience increases in concentrations.

Table 4. Predicted Concentrations of NO_x, NO_2, and PM_{10} for Pre- and Post-CCS Periods[a]

Location[b]	Pre-CCS Concentration	SD	Post-CCS Concentration	SD	Difference
NO_x (ppb)					
Within CCZ	64.3	30.6	60.7	27.2	−3.6
Outside CCZ	35.1	13.7	33.3	12.5	−1.9
Greater London	35.5	14.4	33.6	13.2	−1.9
NO_2 (ppb)					
Within CCZ	29.2	7.1	29.3	7.3	0.1
Outside CCZ	20.0	3.8	19.8	3.9	−0.2
Greater London	20.1	4.0	19.9	4.1	−0.2
PM_{10} (µg/m^3)					
Within CCZ	29.4	6.3	29.0	5.4	−0.4
Outside CCZ	23.8	2.2	24.2	2.0	0.4
Greater London	23.9	2.4	24.2	2.1	0.4

[a] Annual mean concentrations are for the 2 years before (2001 and 2002) and after (2003 and 2004) the CCS was implemented. Averages were calculated from 50,000 model prediction points within the CCZ and from 4.1 million prediction points for the remainder of Greater London.

[b] Outside the CCZ includes Inner and Outer London.

Furthermore, for some areas slight increases in concentrations of NO_x were projected between pre- and post-CCS periods; the most notable was the area immediately west of the CCZ (the area that would be annexed in 2007 as the Western Extension of the CCZ). The reason for this predicted increase in concentrations was likely a consequence of the expected increase in vehicle activity in this area, although again this would require further investigation. Finally, close to major roads where the impact of changes in VKT and emission reductions was likely to have a large effect, NO_x concentrations were predicted to show the largest reduction overall.

The average concentrations summarized in Table 4 show that the predicted difference in NO_x between pre- and post-CCS periods would be −1.9 ppb for both the whole of Greater London and for the area outside the zone. Within the CCZ the projected difference in NO_x concentrations was −3.6 ppb. Because our models predicted a gradient from west to east across Greater London, however, we undertook a further analysis. We summarized NO_x concentrations across a strip of London that was the same width as the CCZ, but did not include it, and ranged between the most northerly and most southerly points of Greater London. In this strip, the change from before to after the CCS for NO_x was estimated to be −1.8 ppb, similar to the Greater London value. Hence, assuming that the Greater London mean reduction in NO_x would also represent the change in NO_x within the CCZ — without including the effect from the CCS — we calculated that the annual mean NO_x concentration within the CCZ would decrease by a net of 1.7 ppb.

The difference map of Greater London for NO_2 (Figure 9) shows a spatial distribution of predicted changes in concentrations different than that for NO_x; London is split into areas showing increased concentrations (in the west) and others with decreased concentrations (in the east), although the absolute changes were very small. Predicting NO_2 concentrations was complicated by our model assumption that primary NO_2 would increase between the pre- and post-CCS periods due to increased retrofitting of diesel vehicles with particle traps. The impact of this

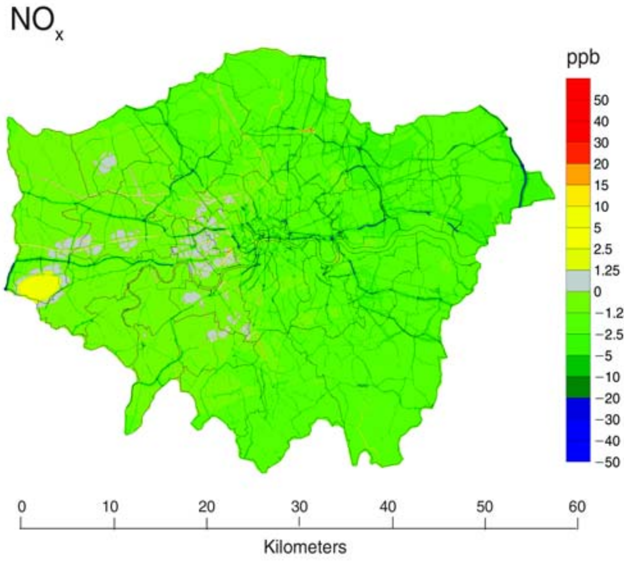


Figure 8. Change in NO_x (ppb) calculated as the modeled level before CCS subtracted from the modeled level after CCS.

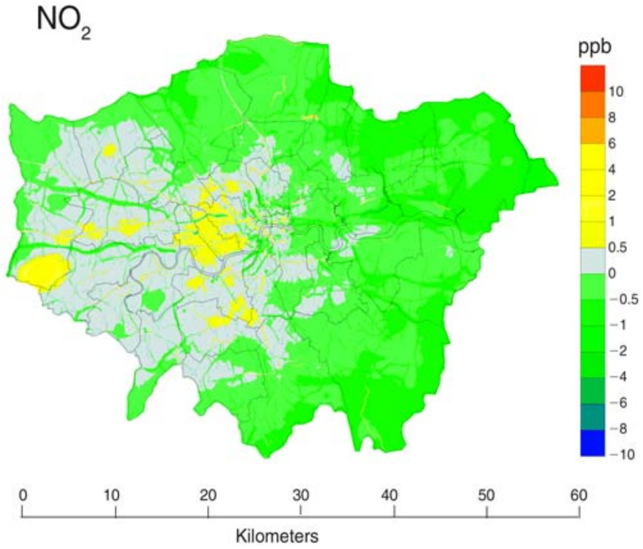


Figure 9. Change in NO_2 (ppb) calculated as modeled level before CCS subtracted from modeled level after CCS.

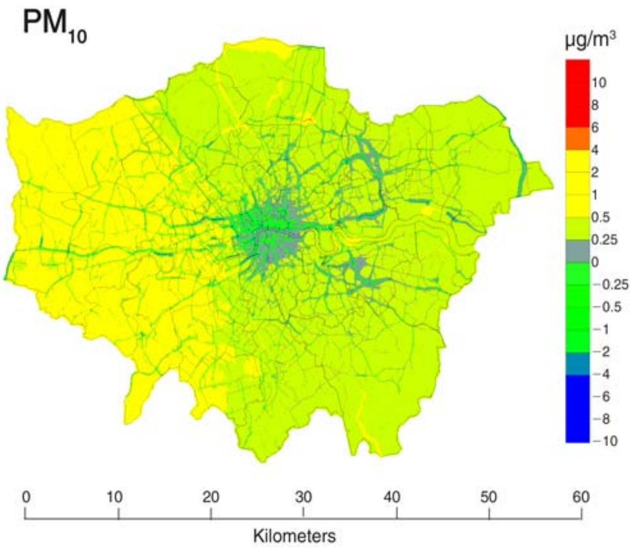


Figure 10. Change in PM_{10} (µg/m³) calculated as modeled level before CCS subtracted from modeled level after CCS.

assumption varied road by road according to the mix of vehicles; those roads with more diesel vehicles or vehicles using particle traps would have predictions of larger increases in NO_2 concentrations than other roads. This was most apparent at roadside sites close to the area that would become the Western Extension of the CCZ and within the CCZ itself. The predicted average NO_2 concentrations in Table 4 suggested that in the area outside the zone as well as in Greater London as a whole, there would be a small reduction in mean NO_2 concentrations. This might be attributable to a combination of lower NO_x and slightly higher primary NO_2. However, within the CCZ we predicted an estimated increase in NO_2 concentrations (0.1 ppb) despite the larger reduction in NO_x. The change in NO_2 within the CCZ was predicted to be very small and not significant; but it was in the opposite direction of the change in NO_x. We assumed this result to be a consequence of increased primary NO_2 within the CCZ.

By comparing the predicted average concentrations for NO_2 within the CCZ and outside the zone, we estimated that the CCS was likely to have annual mean NO_2 concentrations increased by a net 0.3 ppb within the CCZ. This interpretation was supported by our subsequent analysis of roadside measurements within the CCZ, which showed that at Westminster—Marylebone Road NO_x dropped from 166 ppb to 162 ppb whereas NO_2 increased from 43 ppb to 57 ppb for the period before and after CCS implementation. The roadside site at Camden—Shaftesbury Avenue (also in the CCZ) showed similar patterns; NO_x dropped from 93 ppb to 83 ppb, whereas NO_2 remained unchanged at 38 ppb.

The difference map of Greater London for PM_{10} (Figure 10) shows that PM_{10} concentrations were projected to increase slightly between the pre- and post-CCS periods. Once again the model predicted a west-to-east gradient in the changes and we assumed that occurred for the same reasons as those suggested for NO_x concentrations. Some large roads and the CCZ stand out in the plot as having a smaller increase in PM_{10} than elsewhere. Again comparing the absolute changes within the CCZ with those outside the zone, one could estimate that the CCS reduced the annual mean PM_{10} concentration within the CCZ by a net of approximately 0.8 µg/m³. A more detailed modeling analysis of the sources of NO_x and PM_{10} in the CCZ is given in the following section.

Model Sensitivity Tests

We conducted a number of model sensitivity tests (summarized in Table 5) to examine the relative contributions of emissions from areas of London (within the CCZ; Inner, Outer, and External London; and the rural area outside of Greater London) and from vehicular sources (cars, buses, and taxis) to the predicted concentrations of NO_x, NO_2, and PM_{10} under different assumptions about changes in traffic (speed, VKT, composition of fleet).

Before each sensitivity test, we estimated separately the emission contributions from Greater London major roads (local roadside), Greater London minus the major roads (London background), and outside of Greater London (rural).

Table 5. Summary of Model Sensitivity Tests[a]

Model Run	Traffic Flow (CCZ + IRR)	Traffic Speed (CCZ + IRR)	Traffic Flow and Speed in the Remainder of Greater London
Rural	Post-CCS	Post-CCS	Post-CCS
Local roadside	Post-CCS	Post-CCS	Post-CCS
London background	Post-CCS	Post-CCS	Post-CCS
2003 Base case	Post-CCS	Post-CCS	Post-CCS
Speed impact	Post-CCS	Pre-CCS	Post-CCS
Bus impact	Pre-CCS (buses only)	Post-CCS	Post-CCS
Car impact	Pre-CCS (cars only)	Post-CCS	Post-CCS
Taxi impact	Pre-CCS (taxis only)	Post-CCS	Post-CCS
No CCS	Pre-CCS	Pre-CCS	Post-CCS

[a] For the sensitivity analyses, pre-CCS includes data from only 2002 and post-CCS includes data from only 2003.

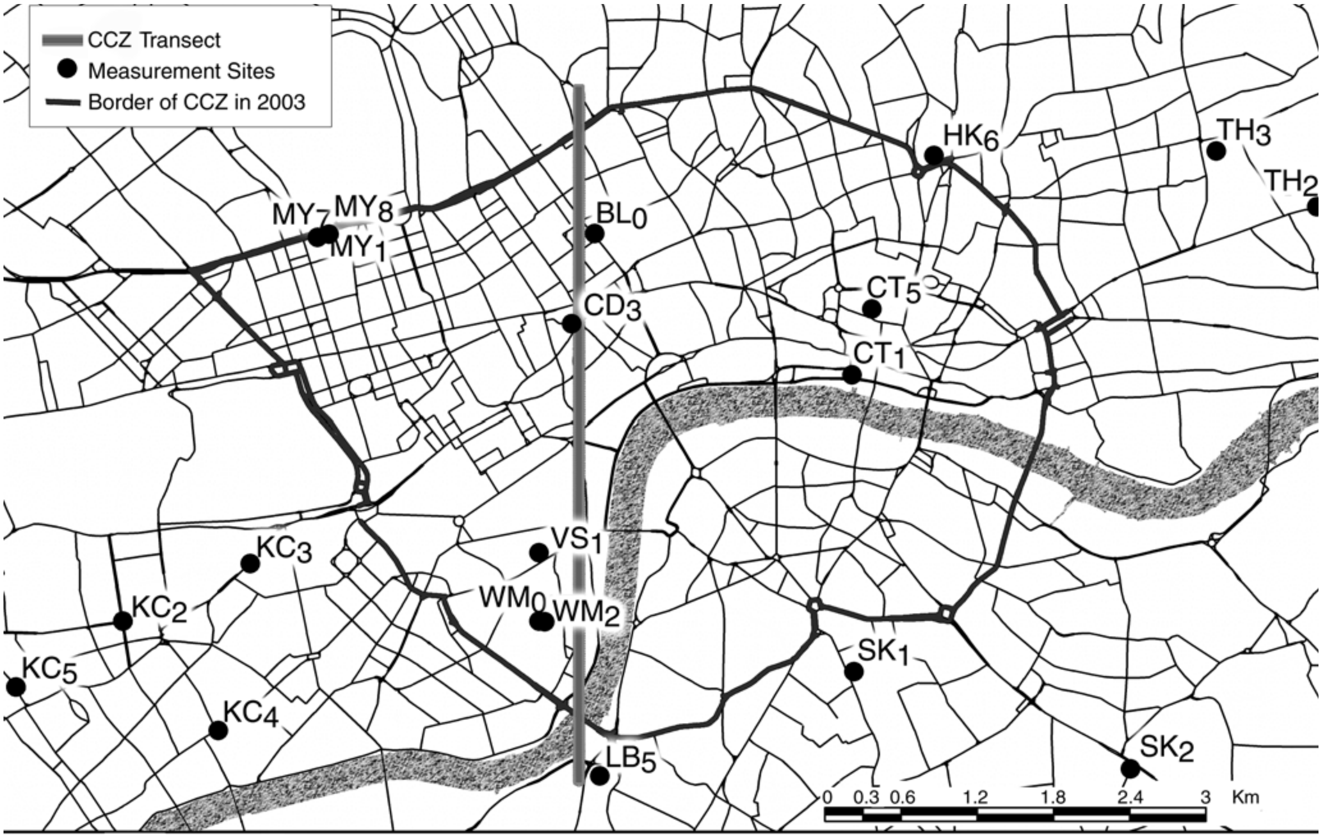


Figure 11. A transect of the CCZ along which modeled predictions were plotted at 20-m intervals. (Some monitoring sites are identified by codes.)

For the pre-CCS period, we used data for only 2002 and for the post-CCS period data for only 2003 so the following assumptions were common to all runs: meteorology, the rural contribution to London's air pollution, emissions from non-vehicle sources, VKT, speed outside the zone (beyond the IRR), and vehicle stock.

The sensitivity tests sought to vary the traffic within the CCZ and on the IRR only, and to assess specifically the flow and speed impacts from key vehicle types.

In the first set of sensitivity tests (the first three in Table 5), each model was run by removing, in turn, the rural contribution to NO_x, then the rural contribution to PM_{10}, and then the local road contribution to each pollutant. The differences in the results between these runs and the results from the 2003 model run (which included all CCS impacts) were assumed to represent the contribution from the remaining component, the London background, which included both non-vehicle and vehicle sources.

The modeled results were then sliced across a north–south transect of the CCZ (Figure 11) and the predicted concentrations of each pollutant and their contributions from rural background, London background, and local roads were plotted at 20-m intervals along the transect. The NO_x and PM_{10} results are summarized in Figures 12 and 13 and show the different components stacked on top of each other. For both figures, the rural contribution is at the bottom in dark grey, the London background contribution is just above it in light grey, and the local roads are on top in black. For the NO_x transect, the rural contribution was relatively small; the majority contribution was from London background and local roads. Because some of the London background also included a road component, emissions from roads were very important for NO_x in the CCZ. In contrast, the dominant source of PM_{10} was predicted to come from the rural area outside of Greater London, whereas concentrations associated with London background and local

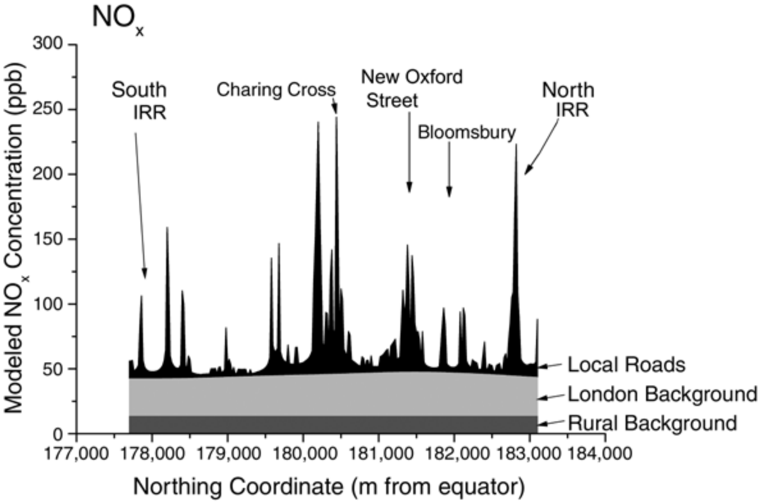


Figure 12. Modeled NO_x source apportionment across the CCZ. IRR at each end of the graph is the boundary for the CCZ.

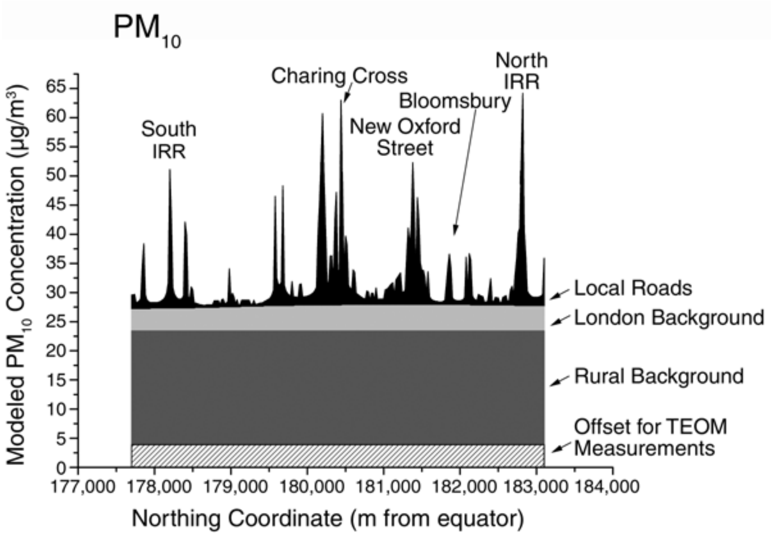


Figure 13. Modeled PM_{10} source apportionment across the CCZ. IRR at each end of the graph is the boundary for the CCZ. The hatched area at the bottom is the offset for measurements made with a tapered element oscillating microbalance (TEOM).

roads were more modest. These results provide important insights for managing air pollution through road traffic schemes and, in particular, for PM_{10} for which the large contribution from rural background suggests that traffic management schemes are limited in their potential impact.

The second set of model sensitivity tests (the remaining six in Table 5) were undertaken to look specifically at the traffic impacts associated with the introduction of the CCS. For example, changes in speed (km/hr) and traffic flow (VKT) within the CCZ and on the IRR for buses, cars, and taxis were incorporated into the model. The base case was a 2003 model run that included all estimated CCS impacts (changes in VKT for cars, buses, and taxis, and changes in speed) and estimates of emissions for each area of Greater London. For the vehicle sensitivity runs, the change in VKT for taxis, buses, and cars was, in turn, returned to its 2002 value keeping all other vehicles (and speeds) the same. For the speed sensitivity test, all vehicle types remained at 2003 flow levels, and the speed was returned to 2002 levels. Finally, a no-CCS run was made with all VKT and speed levels returned to the 2002 values for the CCZ and IRR (see Tables 6 and 7 for emission predictions under a range of traffic assumptions). The results from each sensitivity test were compared with those from the base case and the difference in concentrations was expressed as a percentage of change. The results were plotted on the transect described above and are summarized below.

Table 6. Vehicle NO_x, NO_2, and CO_2 Emissions for All Sensitivity Model Runs Set at 2003 Base Case[a]

Location	Without CCS[b]	Cars Remain at 2002 VKT in CCZ + IRR	Buses Remain at 2002 VKT in CCZ + IRR	Taxis Remain at 2002 VKT in CCZ + IRR	Speed Remains at 2002 VKT in CCZ + IRR	With CCS[b]
NO_x[c]						
Within CCZ	1,271	1,231	1141	1,145	1,261	1,174
Inner London	8,958	8,962	8,944	8,948	8,990	8,956
Outer London	19,185	19,185	19,185	19,185	19,185	19,185
External London	17,153	17,153	17,153	17,153	17,153	17,153
Total London	46,566	46,531	46,423	46,431	46,589	46,468
NO_2						
Within CCZ	205	200	186	192	211	195
Inner London	1,331	1,333	1,329	1,331	1,338	1,332
Outer London	2,673	2,673	2,673	2,673	2,673	2,673
External London	2,257	2,257	2,257	2,257	2,257	2,257
Total London	6,466	6,463	6,445	6,453	6,478	6,458
NO_2/NO_x (%)						
Within CCZ	16.1	16.3	16.3	16.8	16.7	16.6
Inner London	14.9	14.9	14.9	14.9	14.9	14.9
Outer London	13.9	13.9	13.9	13.9	13.9	13.9
External London	13.2	13.2	13.2	13.2	13.2	13.2
Total London	13.9	13.9	13.9	13.9	13.9	13.9
CO_2						
Within CCZ	310,481	299,106	261,582	258,167	287,905	265,253
Inner London	2,447,483	2,446,499	2,441,695	2,440,979	2,451,556	2,442,968
Outer London	5,196,065	5,196,065	5,196,065	5,196,065	5,196,065	5,196,065
External London	3,797,223	3,797,223	3,797,223	3,797,223	3,797,223	3,797,223
Total London	11,751,252	11,738,893	11,696,565	11,692,434	11,732,749	11,701,509

[a] The precision with which the emissions are reported is not meant to reflect the accuracy of the estimate. We estimated that NO_x emission totals had an uncertainty of ± 24% (2 SD). See Appendix D (available on the HEI Web site). Values are shown in metric tonnes (1000 kg or ~2205 pounds) per year.

[b] The difference between with and without CCS also includes the estimates of emissions from LGVs and HGVs.

[c] Examples of estimating emission changes associated with introduction of the CCS using Table 6:

Total NO_x emissions inside the CCZ = (With CCS) − (Without CCS) = 1174 − 1271 = −97 tonnes/year.
Car-related NO_x emissions in the CCZ = 1174 − 1231= −57 tonnes/year.
Bus-related NO_x emissions in the CCZ = 1174 − 1141 = +33 tonnes/year.

The reasons for choosing taxi, car, and bus data were, first, that these vehicle types represent an important contribution to the total emissions in the CCZ; and second, they have undergone the largest changes between the pre- and post-CCS periods. In Table 8, the 2003 emissions are broken down by vehicle type; from these data it can be calculated that emissions from taxis, cars, and buses in the CCZ represented, respectively, 18%, 14%, and 21% of NO_x and 30%,18%, and 6% of PM_{10} (from tire- and brake-wear and exhaust). The changes in traffic flow (VKT) from before to after CCS implementation for taxis, cars, and buses were assumed to be +15.1%, −26.2%, and +15.9%, respectively, and the change in average speed was 2.1 km/hr (TfL 2004).

The CCS impact plots in Figures 14 and 15 show the impacts associated with each sensitivity test. The overall impact of the CCS (traffic flow and speed) is shown in blue, the impact of speed changes for all vehicles in green, and changes in VKT associated with cars in purple, with buses in red, and with taxis in black. It is immediately apparent from the plots that these changes had competing impacts on projected concentrations of individual pollutants at different locations along the transect; for example, higher traffic speeds and fewer cars led to reductions in projected NO_x and PM_{10} concentrations, whereas more VKT by buses and taxis increased concentrations. Projected impacts were particularly noticeable at road intersections. Thus, this analysis suggests that each part of the transect would have a unique CCS impact dependent upon the contribution of different vehicle types at each location. The analysis also supports the efficacy of increasing vehicle speed as a way of reducing vehicle emissions in congested areas, although this is entirely dependent upon the assumed relationship between speed and emissions used in the emissions model.

Table 7. Vehicle PM_{10} Emissions for All Sensitivity Model Runs Set at 2003 Base Case[a]

Location	Without CCS[b]	Cars Remain at 2002 VKT in CCZ + IRR	Buses Remain at 2002 VKT in CCZ + IRR	Taxis Remain at 2002 VKT in CCZ + IRR	Speed Remains at 2002 VKT in CCZ + IRR	With CCS[b]
Total PM_{10}[c]						
Within CCZ	106	105	98	95	105	99
Inner London	724	725	724	724	727	725
Outer London	1390	1390	1390	1390	1390	1390
External London	854	854	854	854	854	854
Total London	3073	3074	3067	3063	3076	3068
Exhaust PM_{10}						
Within CCZ	80	78	76	73	82	76
Inner London	478	479	479	478	481	479
Outer London	873	873	873	873	873	873
External London	600	600	600	600	600	600
Total London	2031	2030	2027	2024	2036	2028
Tire & brake PM_{10}						
Within CCZ	25	26	23	23	23	23
Inner London	246	246	246	246	246	246
Outer London	517	517	517	517	517	517
External London	254	254	254	254	254	254
Total London	1042	1044	1040	1039	1040	1040

[a] The precision with which the emissions are reported is not meant to reflect the accuracy of the estimate. We estimated that PM_{10} exhaust emission totals had an uncertainty of ± 22% (2 SD) and that tire- and brake-wear PM_{10} emission totals had an order of magnitude uncertainty. See Appendix D (available on the HEI Web site). Values are shown in metric tonnes (1000 kg or ~2205 pounds) per year.

[b] The difference between with and without CCS also includes estimates of emissions from LGVs and HGVs.

[c] Examples of estimating emission changes associated with the introduction of the CCS using Table 7:

Total PM_{10} emissions inside the CCZ = (With CCS) − (Without CCS) = 99 − 106 = −7 tonnes/year.
Car-related PM_{10} emissions in the CCZ = 99 − 105 = −6 tonnes/year.
Bus-related PM_{10} emissions in the CCZ = 99 − 98 = +1 tonnes/year.

Table 8. Breakdown of Projected Emissions by Type of Vehicle in 2003[a]

Location	Motor-cycles	Taxis	Cars	Buses and Coaches	LGVs	Rigid HGVs	Articulated HGVs	Routemaster Buses	Total
Exhaust PM_{10}									
Within CCZ	6	23	9	4	13	9	2	4	71
Inner London	28	64	86	20	112	78	30	8	425
Outer London	35	71	185	27	226	134	97	0	777
External London	12	27	114	6	164	77	178	0	578
Tire & Brake PM_{10}									
Within CCZ	1	5	8	2	4	2	0	1	23
Inner London	3	44	121	13	36	23	5	1	246
Outer London	3	77	286	20	69	43	18	0	517
External London	1	30	138	4	33	20	29	0	254
NO_x									
Within CCZ	8	213	167	244	112	256	65	93	1,159
Inner London	35	959	2,216	1,274	972	2,280	866	198	8,801
Outer London	49	1,431	5,925	1,921	1,957	4,280	3,332	10	18,906
External London	21	552	4,901	512	1,305	2,888	6,909	0	17,089
NO_2									
Within CCZ	0	25	15	67	25	36	9	19	195
Inner London	1	93	189	349	220	319	121	40	1,332
Outer London	2	127	496	526	454	599	467	2	2,673
External London	1	49	386	141	309	404	967	0	2,257
CO_2									
Within CCZ	8,461	59,001	90,303	26,590	37,726	27,212	7,651	8,310	265,253
Inner London	32,574	417,141	1,177,209	139,162	310,056	246,222	103,708	16,897	2,442,968
Outer London	36,076	681,515	2,748,558	213,481	598,731	481,456	435,399	848	5,196,065
External London	11,427	263,721	1,773,546	61,285	386,265	349,969	950,982	27	3,797,223

[a] The precision with which the emissions are reported is not meant to reflect the accuracy of the estimate. We estimated that NO_x emission totals had an uncertainty of ±24% (2 SD), PM_{10} exhaust emission totals had an uncertainty of ±22% (2 SD), and PM_{10} tire- and brake-wear emission totals had an order of magnitude uncertainty. See Appendix D (available on the HEI Web site). Values are shown in metric tonnes (1000 kg or ~ 2205 pounds) per year.

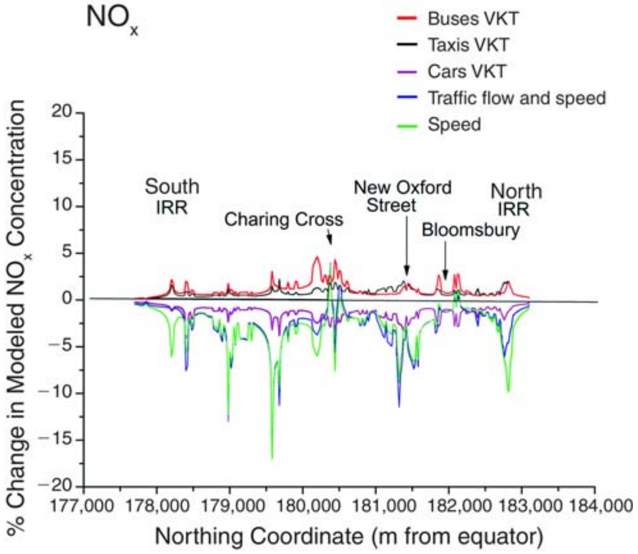


Figure 14. The modeled impacts of the CCS on NO_x concentrations across the CCZ. Graphs are percent changes in NO_x concentrations due to changes in speed (green), traffic flow and speed (blue), VKT for cars (purple), VKT for taxis (black), and VKT for buses (red). IRR at each end of the graph is the boundary for the CCZ.

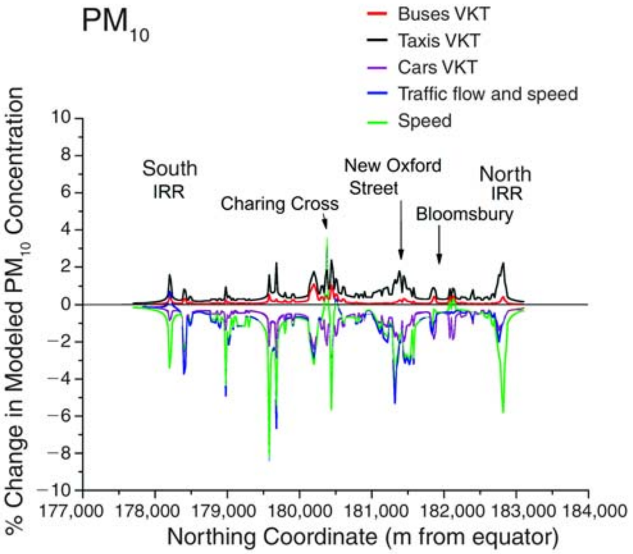


Figure 15. The modeled impacts of the CCS on PM_{10} concentrations across the CCZ. Graphs are percent changes in PM_{10} concentrations due to changes in speed (green), traffic flow and speed (blue), VKT for cars (purple), VKT for taxis (black), and VKT for buses (red). IRR at each end of the graph is the boundary for the CCZ.

NO_x Concentrations

To allow a direct comparison with the later analysis using measurement data, model predictions of pollutant concentrations at the site of key LAQN monitoring stations in the study were averaged arithmetically over the 2 years before and over the 2 years after the implementation of the CCS and expressed as annual means. In order to compare the results of this analysis with those of measured concentrations later, we defined the areas of London differently: We drew a circumference 8 km from the center of the CCZ. The area between the boundary of the CCZ and the 8-km circle was designated as "surrounding the zone"; everything beyond the 8-km circle was designated as "outside the zone" (a control area; Figure 16). Tables 9 through 12 show the predicted annual means of NO_x, NO, NO_2, and PM_{10} before and after the CCS introduction and the percentage of change for each monitoring site in these three areas. Figure 17 plots the percentage of change in each pollutant at individual sites as a function of the distance from the center of CCZ. It should be noted, however, that the model predictions are annual means and not geometric means as are used in the analysis of the measurement data discussed later in the section Analysis of Temporal Changes in Mean Measured Pollutant Concentrations Across London. Also, the modeling analysis could not distinguish between weekday charging hours and weekends, which is later addressed with the measurement data.

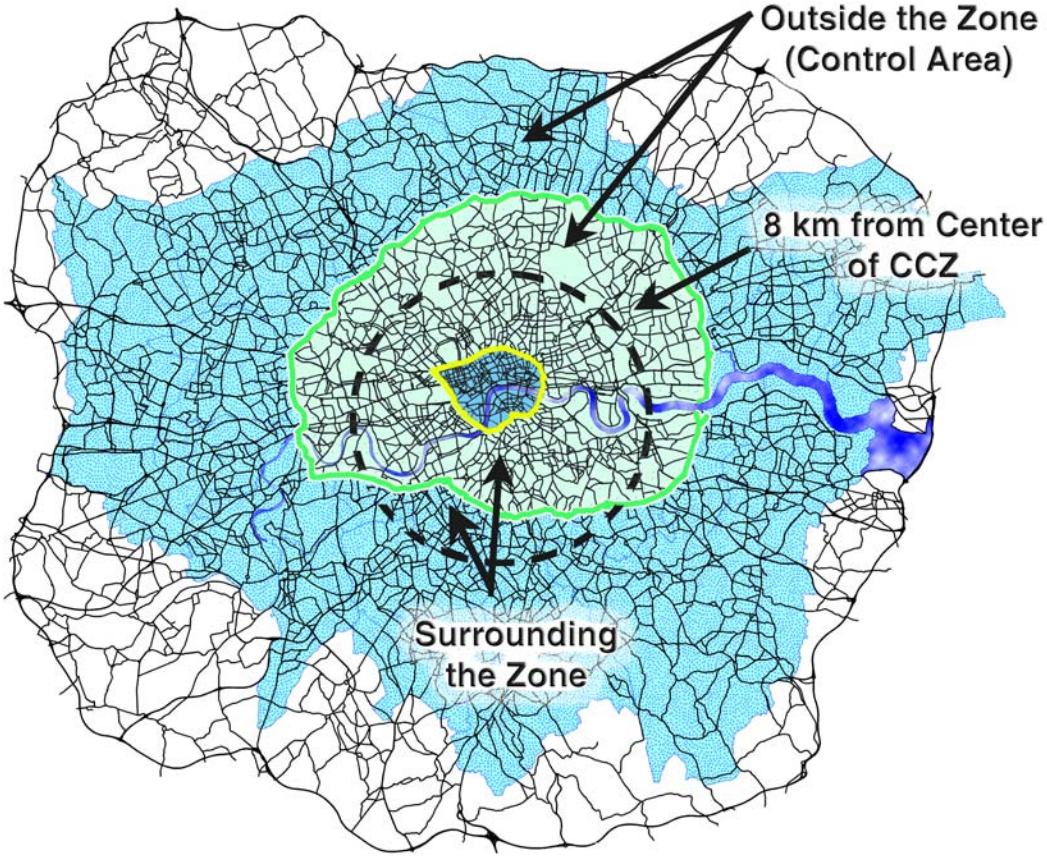


Figure 16. Areas of London designated as within the CCZ, surrounding the zone (between the boundary of the CCZ and the inner boundary of the control area), **and outside the zone** (the control area; at least 8 km from the center of the CCZ and within Greater London).

Table 9. Model Predictions for NO_x at Air Pollution Monitoring Sites[a]

Monitoring Site	Distance from Center of CCZ (km)	Annual Mean Before CCS (ppb)	Annual Mean After CCS (ppb)	% Change
Within CCZ				
Bloomsbury—Russell Square	1.5	50.9	49.8	−2.1
City of London—Senator House	1.5	61.7	58.6	−5.0
Westminster—Horseferry Road	1.9	51.8	49.5	−4.4
Surrounding the Zone[b]				
Southwark—Elephant and Castle	2.5	62.0	57.5	−7.2
Islington—Upper Street	3.6	48.7	46.9	−3.6
Tower Hamlets—Bethnal Green	4.8	47.3	45.6	−3.7
West London—AURN	6	47.0	47.0	0.0
Tower Hamlets—Poplar	6.7	43.3	40.1	−7.5
K & C—North Kensington	6.9	44.9	45.3	0.8
Hackney—Clapton	7	48.1	44.8	−6.8
Wandsworth—Town Hall	7.8	55.4	53.8	−2.8
Outside the Zone[c]				
Waltham Forest—Dawlish Road	9.7	40.7	39.4	−3.3
Lewisham—Catford	9.8	55.3	52.1	−5.8
Barnet—Finchley	11.1	36.0	34.7	−3.5
Ealing—Ealing Town Hall	13.4	45.7	46.0	0.6
Enfield—Salisbury School	15.1	29.2	27.0	−7.8
Redbridge—Perth Terrace	15.3	35.0	32.5	−7.1
Harrow—Stanmore	17.3	27.6	26.6	−3.6

[a] Only sites that existed for all 4 years and had a data-capture rate of > 75% were included in this analysis.

[b] Surrounding the zone is from the boundary of the CCZ out to 8 km from the CCZ center.

[c] Outside the zone (control area) is beyond 8 km from the CCZ center and within Greater London.

DISCUSSION

These analyses of CCS impacts on emissions and air pollution were based upon emissions inventory and dispersion modeling approaches and were aimed at providing an estimate of the impact of introducing the CCS.

The Physical Properties of the CCS Area

The CCZ is a relatively small proportion of the area of London (approximately 1.4%). The impacts of any changes within the CCZ were therefore a combination of changes to local road traffic combined with changes in other parts of London. For emissions, the portions attributed to the CCZ were also relatively small; for example, for NO_x in 2002 the CCZ represented 4.2% of London's total road traffic emissions, for NO_2 it was 4.8%, and for CO_2 it was 4.0%. The CCZ did however have the highest NO_2-to-NO_x emissions ratio in the London area and was 15% above the London average. PM_{10} emissions within the CCZ as a proportion of total emissions were similarly small; the CCZ represented 4.9% of total PM_{10} (both exhaust and tire- and brake-wear emissions), 5.7% of exhaust emissions, and 3.3% of tire- and brake-wear emissions.

The Representation of Road Traffic As a Proportion of All Emissions in London and Predicted Trends

In 2002 the modeling results showed that, for the whole LAEI area, road traffic contributed 55% of total NO_x emissions, 77% of PM_{10} emissions, and 30% of CO_2 emissions.

Emissions of NO_x for London were estimated to drop from 57,751 tonnes/year in 2001 to 42,613 tonnes/year in 2004 (26%; Table 2). Over the same period, NO_2 emissions were predicted to drop from 6888 tonnes/year to 6454 tonnes/year (only 6%) and hence the NO_2:NO_x emissions ratio was predicted to increase from 11.9% to 15.1%. Over

Table 10. Model Predictions for NO at Air Pollution Monitoring Sites[a]

Monitoring Site	Distance from Center of CCZ (km)	Annual Mean Before CCS (ppb)	Annual Mean After CCS (ppb)	% Change
Within CCZ				
Bloomsbury—Russell Square	1.5	25.0	23.5	−6.0
City of London—Senator House	1.5	32.6	29.4	−9.9
Westminster—Horseferry Road	1.9	25.7	23.4	−9.0
Surrounding the Zone[b]				
Southwark—Elephant and Castle	2.5	32.6	28.1	−13.5
Islington—Upper Street	3.6	23.6	21.6	−8.4
Tower Hamlets—Bethnal Green	4.8	22.7	20.8	−8.1
West London—AURN	6	22.5	21.8	−2.9
Tower Hamlets—Poplar	6.7	20.1	17.4	−13.8
K & C—North Kensington	6.9	21.0	20.7	−1.6
Hackney—Clapton	7	23.4	20.5	−12.3
Wandsworth—Town Hall	7.8	28.5	26.5	−6.9
Outside the Zone[c]				
Waltham Forest—Dawlish Road	9.7	18.2	16.8	−7.8
Lewisham—Catford	9.8	28.4	25.3	−11.0
Barnet—Finchley	11.1	15.1	13.9	−8.2
Ealing—Ealing Town Hall	13.4	21.8	21.4	−1.8
Enfield—Salisbury School	15.1	11.0	9.3	−15.5
Redbridge—Perth Terrace	15.3	14.6	12.6	−14.0
Harrow—Stanmore	17.3	10.0	9.1	−9.2

[a] Only sites that existed for all 4 years and had a data-capture rate of > 75% were included in this analysis.

[b] Surrounding the zone is from the boundary of the CCZ out to 8 km from the CCZ center.

[c] Outside the zone (control area) is beyond 8 km from the CCZ center and within Greater London.

the same period, PM_{10} total emissions (from exhaust and tire and brake wear) were predicted to drop from 3602 tonnes/year to 2861 tonnes/year (21%; Table 3). However, whereas PM_{10} from exhaust was predicted to drop by 29%, PM_{10} from tire and brake wear was predicted not to change; hence, the contribution from tire and brake wear to total vehicle PM_{10} emissions increased from 29% to 36%. If these predictions were to be reflected in actual ambient concentrations, they could have important policy implications for controlling atmospheric concentrations of PM_{10}. As a proportion of total vehicle PM_{10}, emissions from tire and brake wear were projected to be lower in the CCZ (22.8%) averaged over the 4 years of the study than the London mean value (32.5%).

Between the years 2002 and 2003, the changes in emissions for the CCZ were predicted to be −14% for NO_x, −5% for NO_2, −16% for PM_{10}, and −17% for CO_2 (Tables 2 and 3). However these reductions reflect a combination of the changes in VKT and vehicle speed and the improvements in the emissions performance of the vehicle fleet.

The Ability of Small Numbers of Measurement Sites to Reflect Complex Urban Traffic Management Changes

The LAPT transect plots for NO_x and PM_{10} (Figures 12 and 13) show that the contribution made by road traffic at any location was unique; therefore modeled changes that might be brought about by the CCS varied depending on the road and upon contributions from local sources. The consequence of this inference for studying traffic management schemes is that analysis of measurement data from any single roadside site within the CCZ cannot be assumed to reflect the overall impact of the CCS.

One solution for this problem is including background monitoring sites because they have a more consistent source attribution; but they also have the possible limitation of a

Table 11. Model Predictions for NO_2 at Air Pollution Monitoring Sites[a]

Monitoring Site	Distance from Center of CCZ (km)	Annual Mean Before CCS (ppb)	Annual Mean After CCS (ppb)	% Change
Within CCZ				
Bloomsbury—Russell Square	1.5	25.9	26.3	1.7
City of London—Senator House	1.5	29.0	29.2	0.5
Westminster—Horseferry Road	1.9	26.0	26.1	0.2
Surrounding the Zone[b]				
Southwark—Elephant and Castle	2.5	29.4	29.4	−0.1
Islington—Upper Street	3.6	25.1	25.3	0.8
Tower Hamlets—Bethnal Green	4.8	24.7	24.7	0.3
West London—AURN	6.0	24.5	25.2	2.7
Tower Hamlets—Poplar	6.7	23.2	22.7	−2.1
K & C—North Kensington	6.9	23.9	24.6	3.0
Hackney—Clapton	7.0	24.6	24.3	−1.5
Wandsworth—Town Hall	7.8	26.9	27.3	1.6
Outside the Zone[c]				
Waltham Forest—Dawlish Road	9.7	22.5	22.6	0.4
Lewisham—Catford	9.8	26.9	26.8	−0.4
Barnet—Finchley	11.1	20.8	20.8	−0.1
Ealing—Ealing Town Hall	13.4	23.9	24.5	2.7
Enfield—Salisbury School	15.1	18.2	17.6	−3.0
Redbridge—Perth Terrace	15.3	20.4	19.9	−2.3
Harrow—Stanmore	17.3	17.6	17.5	−0.4

[a] Only sites that existed for all 4 years and had a data-capture rate of > 75% were included in this analysis.

[b] Surrounding the zone is from the boundary of the CCZ out to 8 km from the CCZ center.

[c] Outside the zone (control area) is beyond 8 km from the CCZ center and within Greater London.

Table 12. Model Predictions for PM_{10} at Air Pollution Monitoring Sites[a]

Monitoring Site	Distance from Center of CCZ (km)	Annual Mean Before CCS (µg/m^3)	Annual Mean After CCS (µg/m^3)	% Change
Within CCZ				
Bloomsbury—Russell Square	1.5	26.6	26.7	0.4
Surrounding the Zone[b]				
Islington—Upper Street	3.6	25.7	25.8	0.3
Tower Hamlets—Poplar	6.7	25.3	25.4	0.4
K & C—North Kensington	6.9	24.8	25.3	2.2
Outside the Zone[c]				
Waltham Forest—Dawlish Road	9.7	24.3	24.7	1.4
Barnet—Finchley	11.1	23.6	24.1	1.9
Enfield—Salisbury School	15.1	23.0	23.4	1.7
Redbridge—Perth Terrace	15.3	23.6	23.9	1.3
Harrow—Stanmore	17.3	22.6	23.1	2.4

[a] Only sites that existed for all 4 years and had a data-capture rate of > 75% were included in this analysis.

[b] Surrounding the zone is from the boundary of the CCZ out to 8 km from the CCZ center.

[c] Outside the zone (control area) is beyond 8 km from the CCZ center and within Greater London.

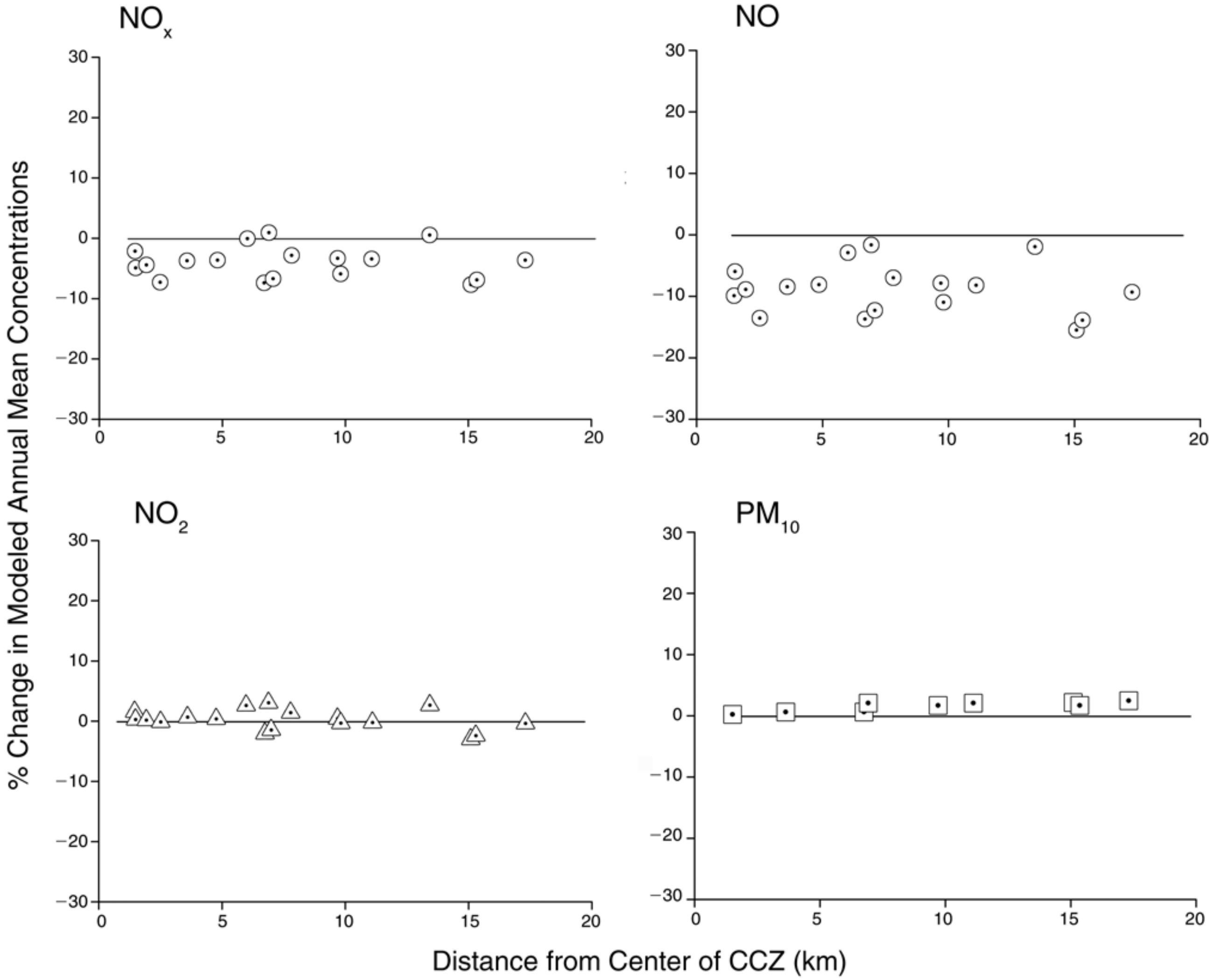


Figure 17. Percentage of difference for NO$_x$, NO, NO$_2$, and PM$_{10}$ as the distance from the center of the CCZ increases.

much smaller local traffic component within the data. An additional complication can be that any small change brought about by the CCS may compete with contributions similar in magnitude from outside the zone. This makes the assessment of any impact on air pollution very difficult to establish.

The model transect plots show that, compared with NO$_x$, PM$_{10}$ is expected to have a much larger component that originated from outside the Greater London area compared with the locally generated traffic contribution (Figures 12 and 13). Hence changes such as those that might be brought about by the CCS are likely to result in a small absolute change in PM$_{10}$ concentration. A possible solution to the problem this dominance by regional background poses for identifying the impact of the CCS, and one that has not been undertaken in this project, would be to compare the London incremental change in PM$_{10}$ (London PM$_{10}$ − rural PM$_{10}$) or, where there are greater numbers of roadside sites, the roadside incremental change in PM$_{10}$ (roadside PM$_{10}$ − nearby background PM$_{10}$). This would possibly provide a more distinguishable signal associated with any traffic changes.

Model Impact Assessment: Before Versus After CCS Introduction

The difference map of Greater London (Figure 8) suggests that predicted NO$_x$ concentrations would fall between pre- and post-CCS periods. The differences between predicted concentrations of NO_x, averaged both across Greater London and across the area outside the zone, were both projected to be −1.9 ppb (Table 4). In contrast, within the CCZ the difference in NO_x concentrations was −3.6 ppb. Assuming that without the CCS impacts the change in NO_x in the CCZ would be approximately the same as the Greater London value, one would conclude that the net impact of the CCS would be to reduce NO_x by an average of 1.7 ppb within the CCZ.

The difference map for NO_2 (Figure 9) shows a similar spatial distribution of concentration changes to those of NO_x, although the absolute changes were very small. In addition, predicting NO_2 concentrations was complicated by the fact that between the pre- and post-CCS periods, a small increase in primary NO_2 was projected (based on assumptions about retrofitting diesel vehicles with particle traps) and that this varied on a road-by-road basis. In the Greater London area as well as outside the zone, a small reduction in NO_2 concentration was estimated that resulted from a combination of reducing NO_x and a small increase in primary NO_2. However within the CCZ there was an estimated increase in NO_2 concentration (0.1 ppb; Table 4) despite the reduction in NO_x. The absolute change in NO_2 was predicted to be very small but in the opposite direction to NO_x and was assumed to be as a consequence of increasing primary NO_2 within the CCZ. Comparing the average concentrations for NO_2 within and outside the zone one would estimate that the net effect of the CCS could have increased the average NO_2 concentration by 0.3 ppb within the CCZ.

The difference map for PM_{10} (Figure 10) shows that PM_{10} is likely to increase slightly between the pre- and post-CCS periods. Comparing the average concentrations for PM_{10} within and outside the zone, one would conclude that the net effect of the CCS was to reduce the average PM_{10} concentrations by 0.8 µg/m³ within the CCZ.

Model Impact Assessment: Impact of Each Vehicle Type

A comparison was also made of the modeled individual impacts that different vehicle types might contribute to the overall changes in NO_x and PM_{10} brought about by the CCS. In summary, decreases in pollutant concentrations were associated with the changes in vehicle speed and the VKT changes of cars. Increases in NO_x and PM_{10} concentrations were those associated with increases in bus and taxi VKTs. Overall the resulting change in air pollutant concentrations was predicted to vary by location in the CCZ dependent upon the contribution of different vehicle types and other pollutant sources at each location. A comparison among the impacts of each vehicle type on air pollution concentrations in 2003 resulted in the following outcomes:

NO_x: −2.5% (overall CCS impact), −2.8% (speed), −1.3% (car), + 1.1% (bus), + 0.8% (taxi);

PM_{10}: −0.9% (overall CCS impact), −1.0% (speed), −0.7% (car), + 0.2% (bus), + 0.5% (taxi).

It is also worth noting that the impact on PM_{10} of increased bus use was limited by the assumption of extensive use of particle traps on these vehicles (Appendix Table D.4).

ESTABLISHING A CCS STUDY DATABASE OF AIR QUALITY MEASUREMENTS

INTRODUCTION

Fixed continuous air quality monitoring within Greater London is primarily driven by local and legislative requirements under the jurisdiction of the 33 London Boroughs. As of February 2003, they funded 91 monitoring sites. In addition, 10 monitoring sites in Greater London were funded by the national government as part of the U.K. Automatic Urban and Rural Network (AURN); and 1 site was funded by the British Airports Authority at London Heathrow Airport.

Measurements made at these 102 monitoring sites are routinely compiled in the LAQN database. The database holds pollutant data of robust quality at either 15-minute, hourly, or daily mean resolution depending on the pollutant and monitoring method. Many of these monitoring sites also record meteorologic parameters. The LAQN database is a source for public dissemination of air quality bulletins and a resource for researchers and local and national governments (see, for example, *www.londonair.org.uk*).

To support the analysis of the impact of the CCS on air quality, the CCS Study Database was tailored to this project and established using ratified measurements obtained from the LAQN database. A statistical and physical description of each of the key indicator sites, including data quality and capture rates, is presented to provide a reference upon which interpretation of results may be based.

SELECTION OF MONITORING SITES

In forming the CCS Study Database, certain “key indicator sites” were identified as being of primary importance. They include all long-term continuous monitoring sites within the CCZ, in Inner London (i.e., the area surrounding the CCZ), and a representative sample of control sites from suburban areas in Outer London (See Figure 4). In the CCS database, these continuous monitoring sites are grouped into six “indicator classes” (Table 13):

Within CCZ–Roadside
Within CCZ–Urban Background
IRR–CCZ Boundary
Inner London–Roadside
Inner London–Urban Background
Suburban Outer London

Table 13. Key Indicator Sites Grouped into Indicator Classes

Monitoring Site	Pollutants Monitored	Monitoring Start Date
Within CCZ–Roadside		
Camden—Shaftesbury Avenue	NO_x, PM_{10}	April 2000
Westminster—Victoria Street	NO_x, CO, (PM_{10}, $PM_{2.5}$ gravimetric)	April 2003
Within CCZ–Urban Background		
Bloomsbury—Russell Square	NO_x, PM_{10}, $PM_{2.5}$, CO	Jan 1993
City of London—Senator House	NO_x	October 2001
City of London—Guildhall	Black smoke	April 1972
Westminster—Horseferry Road	NO_x, CO	July 2001
Westminster—Grosvenor	Black smoke	April 1986
IRR–CCZ Boundary		
Hackney—Old Street	NO_x, PM_{10}	November 2002
Westminster—Marylebone Road	NO_x, PM_{10}, $PM_{2.5}$, CO, black smoke	May 1997
Inner London–Roadside		
Camden—Swiss Cottage	NO_x, PM_{10}	April 1996
K & C—Cromwell Road	NO_x, PM_{10}, CO	May 1998
K & C—Knightsbridge	NO_x	September 2000
K & C—King’s Road	NO_x	March 2000
Lewisham—New Cross	NO_x, PM_{10}	April 2002
Southwark—Old Kent Road[a]	NO_x, PM_{10}, CO	May 1994
Tower Hamlets—Mile End Road	NO_x, CO	March 1993
Wandsworth—High Street	NO_x, PM_{10}, CO	February 1998
Inner London–Urban Background		
Islington—Upper Street	NO_x, PM_{10}	May 1994
K & C—North Kensington	NO_x, PM_{10}, CO	March 1995
K & C—Pembroke Road	NO_x, CO	January 1993
Southwark—Elephant and Castle[a]	NO_x, PM_{10}, CO	May 1993
Tower Hamlets—Poplar[a]	NO_x, PM_{10}	February 1994
Tower Hamlets—Bethnal Green	NO_x, PM_{10}	October 1999
Suburban Outer London		
Bexley—Belvedere[a]	NO_x, PM_{10}, CO	January 1998
Bexley—Slade Green[a]	$PM_{2.5}$	May 1994
Brent—Kingsbury[a]	NO_x, PM_{10}, CO	January 1996
Enfield—Bush Hill Park	Black smoke	January 1990
Greenwich—Eltham[a]	NO_x, PM_{10}	January 1994
Greenwich—Woolwich	Black smoke	January 1990
Mole Valley—Lower Ashstead	NO_x, PM_{10}	April 1997
Redbridge—Ilford	Black smoke	January 1990
Richmond-upon-Thames—Teddington	NO_x	August 1996

[a] Meteorologic parameters were also monitored.

Due to the sensitivity of the analyses being conducted in this study, high data-capture rates were essential. A number of data series from the key indicator sites had low data-capture rates caused by delayed commissioning dates, long-term analyzer faults, or interference from unrelated sources such as road or building work. For example, two sites, Hackney—Old Street (IRR–CCZ Boundary) and Westminster—Victoria Street (Within CCZ–Roadside) were not suitable for most analyses because they were commissioned less than 1 year before the CCS was implemented. For data from the key monitoring sites that were excluded during the ratification process owing to analyzer malfunction, different methods of retrieving measurements were investigated. None of these methods was robust enough to provide adequate certainty of the measurements in light of the very small signal expected for the effects of the CCS on pollution levels. Such sites were either excluded from the analyses or, where appropriate, included with caveats attached to results and conclusions. Footnotes on Tables 14 through 19 provide brief explanations for sites that recorded valid measurements for < 75% of the total number of hourly means during the pre-CCS or post-CCS analysis period. Further information can be obtained from Broughton (2001), Eaton (2006), and Vallence-Plews (2001, 2003, 2004, 2005). As a general rule, all suburban background and roadside sites in Greater London with a data-capture rate of at least 75% (based on hourly means) were included. As an exception, all monitoring sites within the CCZ or on its boundary (the IRR) were included regardless of data-capture rates due to the limited availability of sites in this area.

To aid our analysis, we formed a suburban composite time series of data using the average hourly mean concentrations of all sites in the Suburban Outer London indicator class. This comprised a total of 9 distinct sites including 5 for NO_x, NO, and NO_2; 4 for PM_{10}; 1 for $PM_{2.5}$; 2 for CO; and 3 for black smoke. The method of using the mean concentration of a number of sites minimized the risk of gaps in the dataset through equipment failure and smoothed out noise caused by sources of pollution local to each suburban monitoring site. The suburban sites were sufficiently distant from the CCZ to allow the assumption that changes in pollution measurements due to the CCS would be negligible at these sites.

In addition to the indicator sites, we included many other background and roadside monitoring sites in Suburban Outer London. These sites became an important component of the time-series analysis method we used to identify rates of change within the CCZ and to compare them with those of an Outer London control area (see the section Analysis of Temporal Changes in Mean Measured Pollutant Concentrations Across London). Measurements from these additional sites were used to produce a London-wide trend independent from the effects of the CCS. For this analysis, data from all fixed background and roadside monitoring sites within the LAQN were used (excluding sites specifically classified as “suburban” or “curbside”). A list of the sites and monitoring periods used in that analysis, along with their approximate distance from the center of the CCZ, is included in Appendix B. More details on the inclusion criteria for the time-series analysis method are included in the next section.

SITE CLASSIFICATION DEFINITIONS

United Kingdom standard site classifications as defined in the official Technical Guidance document LAQN TG(03) (U.K. Department for Environment, Food and Rural Affairs [DEFRA] 2003) are used throughout this report:

- Rural. An open countryside location, in an area of low population density distanced as far as possible from roads and populated and industrial areas.
- Suburban. A location in a residential area on the outskirts of a town or city with no major sources of pollution within 50 m.
- Urban Background (also referred to as background). An urban location with no major sources of pollution within 50 m and broadly representative of city-wide background conditions; for example, urban residential areas.
- Roadside. A site sampling between 1 m from the curbside of a busy road and the back of the pavement (sidewalk). Typically this is within 5 m of the road, but could be up to 15 m.
- Curbside. A site sampling within 1 m of the curb of a busy road.

MONITORED POLLUTANTS

The most widespread pollutant species monitored in the LAQN are NO_x and NO_2 (see Table 13). Ozone monitoring is well represented in background and suburban locations; SO_2 monitoring is less widespread and typically limited to locations close to industrial sources. Ambient CO concentrations in London are now well below health standards and monitoring is uncommon, confined almost exclusively to roadside locations. Particulate monitoring in London has increased rapidly in recent years and is dominated by measuring the PM_{10} fraction; most of the monitoring is done using tapered element oscillating microbalances (TEOMs) and about 30% by beta attenuation monitors. The TEOM’s use of a heated element causes loss of the volatile fraction of PM (Green and Fuller 2006). Because data from all key indicator sites used in this study were collected with the TEOM method, an assessment of changes in this volatile fraction could not be made from this dataset.

Increased monitoring of $PM_{2.5}$ via TEOM is relatively recent, increasing from 6 monitors in 2000 to 12 by the end of 2005. Long-term semi-automatic black smoke measurements have been phased out over the past 10 years and only one site remains.

In addition to measurements of these mainstream pollutants, a small number of additional metrics were used: particle size and number, particle mass by gravimetric method, hydrocarbons speciated by gas chromatography, and heavy metals in PM_{10}. These measurements are typically taken at research sites such as Westminster—Marylebone Road (on the CCZ boundary).

Continuous monitoring of pollutant levels for the specific purpose of observing changes caused by the introduction of the CCS had not been established before it was implemented. Measurements were taken at existing sites that did not precisely fit the needs of this study. Furthermore, although continuous monitoring in Greater London is relatively dense compared with other major cities in Europe, the CCZ is only a small fraction of Greater London. Consequently, only a limited number of monitoring sites had been established within the CCZ and roadside $PM_{2.5}$ and black smoke were not measured. The study accommodated these recognized limitations to the extent possible.

QUALITY ASSURANCE AND QUALITY CONTROL OF MEASUREMENTS

All continuous pollutant monitors that contributed data to the CCS database had undergone a process of equipment selection, site selection, equipment maintenance, and calibration; and the measurements had been scaled, validated, and ratified according to the relevant national technical guidance (U.K. DEFRA 2003) before their use in this study. Ratification of black smoke data was subject to a long delay. Consequently, black smoke measurements taken after March 2004 were considered provisional at the time of our analysis, whereas all other pollutant measurements had been fully ratified. Quality assurance and quality control procedures for LAQN monitoring sites followed a defined ratification procedure equal to that of AURN.

CCS STUDY DATABASE STRUCTURE AND ANALYSIS

The analytical framework of the CSS database was based on the structured query language (SQL) software platform. A dedicated SQL database was created on a secure server with full daily backup. Fully ratified 15-minute mean concentrations for CO, NO, NO_2, NO_x, PM_{10}, $PM_{2.5}$, and black smoke from each CCS site were copied from the main LAQN database. Data covered the period from February 17, 2001, through February 16, 2005, corresponding to 2 years before and 2 years after the CCS was introduced. Meteorologic data were added from representative sites in Suburban Outer London. The CCS database held over 14 million pollutant data records.

Summary data were extracted to statistical software by user-defined SQL queries. This allowed rapid repeat analysis by adjusting and rerunning stored queries. This method also limited the possibility of data version conflicts as each analysis was run on the core database, rather than on data that had been extracted to a series of spreadsheets or satellite databases.

SUMMARY STATISTICS

Summary statistics for the concentrations of NO_x, NO_2, PM_{10}, $PM_{2.5}$, CO, NO, and black smoke at each of the indicator sites before and after the CCS are shown in Tables 14 through 19. These statistics were hourly arithmetic means (except for black smoke, which were based on daily means) collected during the 2 years before and after introduction of the CCS. Data were not included for those sites and pollutant species that failed to meet the 75% capture-rate requirement because including them could have led to misinterpretation; footnotes on each table provide brief explanations of excluded data. Appendix G (available on HEI's Web site) describes each of the indicator sites and includes aerial-view photographs of key sites within the CCZ and on the IRR. Capture rates are also shown for each pollutant for the 2-year period before and after the CCS was introduced.

The summary statistics reveal low capture rates for NO_x measurements at one of the background sites within the CCZ (Table 14). Methods to fill substantial data gaps at these key sites were investigated using comparisons with historical data, other species, and neighboring sites. All were considered insufficiently accurate and robust given that the change due to the CCS intervention was predicted to be small. The time-series charts in Appendix G show the distribution of missing data points at these sites.

These statistics also provide an impression of changes in pollutant concentrations between the pre- and post-CCS periods; such impressions were noted before any other detailed analyses were conducted to account for confounding factors such as meteorology or long-term trends independent of the CCS.

Mean concentrations of NO_x, NO, and NO_2 at Suburban Outer London sites appeared level during the pre- and post-CCS periods (Tables 14 [NO_x], 15 [NO], and 16 [NO_2]). NO concentrations at all other sites decreased by 6% to 20%. Camden—Shaftesbury Avenue (Within CCZ–Roadside) recorded a decrease of 14% for NO.

Table 14. Summary Statistics for NO_x Measurements for the 2 Years Before and After the CCS Started[a]

	Mean (ppb)		98th Percentile (ppb)		Capture Rate (%)	
Monitoring Site	Pre	Post	Pre	Post	Pre	Post
Within CCZ–Roadside						
Camden—Shaftesbury Avenue	90	83	243	222	97	94
Westminster—Victoria Street	n.a.[b]	96.8	n.a.[b]	244	0[b]	68
Within CCZ–Urban Background						
Bloomsbury—Russell Square	52	52	160	146	84	87
City of London—Senator House	n.a.[c]	47	n.a.[c]	148	62[c]	84
Westminster—Horseferry Road	n.a.[d]	42	n.a.[d]	125	71[d]	77
IRR–CCZ Boundary						
Hackney— Old Street	n.a.[e]	78	n.a.[e]	207	12[e]	89
Westminster—Marylebone Road	164	163	430	445	94	94
Inner London–Roadside						
Camden—Swiss Cottage	n.a.[f]	n.a.[g]	n.a.[f]	n.a.[g]	46[f]	35[g]
K & C—Cromwell Road	102	100	248	254	96	94
K & C—Knightsbridge	122	120	385	398	96	97
K & C—King's Road	132	128	333	321	96	89
Lewisham—New Cross	n.a.[h]	80	n.a.[h]	235	43[h]	98
Southwark[a]—Old Kent Road	84	73	230	206	88	93
Tower Hamlets—Mile End Road	106	87	297	254	93	95
Wandsworth—High Street	56	52	217	204	96	95
Inner London–Urban Background						
Islington—Upper Street	42	41	159	152	96	93
K & C—North Kensington	36	36	152	148	96	93
K & C—Pembroke Road	44	45	150	152	97	96
Southwark—Elephant and Castle	51	47	153	147	83	86
Tower Hamlets—Poplar	35	32	137	140	95	94
Tower Hamlets—Bethnal Green	40	37	150	137	92	76
Suburban Outer London						
Bexley—Slade Green	30	33	131	154	93	91
Brent—Kingsbury	29	29	142	157	96	93
Greenwich—Eltham	27	27	118	118	96	95
Mole Valley—Lower Ashstead	23	22	110	104	96	97
Richmond-upon-Thames—Teddington	22	21	109	105	96	93
Suburban Composite	26	26	—	—	100	100

[a] Values are based on hourly mean concentrations. Where capture rate was < 75% for either the before or after period, n.a. (not acquired) and a footnote describe major periods of data loss.

[b] Site reopened April 2003 after a 3-year closure.

[c] Site opened October 2002.

[d] Site opened July 2001.

[e] Site reopened November 2002 after a 2-year closure.

[f] Data excluded February 2002 to July 2003 due to baseline clipping of NO_x channel (dual chamber analyzer).

[g] Data excluded January 2004 to May 2004 due to blocked ozone orifice.

[h] Site opened April 2002.

Table 15. Summary Statistics for NO Measurements for the 2 Years Before and After the CCS Started[a]

	Mean (ppb)		98th Percentile (ppb)		Capture Rate (%)	
Monitoring Site	Pre	Post	Pre	Post	Pre	Post
Within CCZ–Roadside						
Camden—Shaftesbury Avenue	53	46	181	160	97	94
Victoria Street—Westminster	n.a.[b]	79	n.a.[b]	213	0[b]	68
Within CCZ–Urban Background						
Bloomsbury—Russell Square	n.a.[c]	22	n.a.[c]	98	43[c]	87
City of London—Senator House	n.a.[d]	19	n.a.[d]	102	62[d]	84
Westminster—Horseferry Road	n.a.[e]	18	n.a.[e]	94	71[e]	83
IRR–CCZ Boundary						
Hackney—Old Street	n.a.[f]	46	n.a.[f]	151	12[f]	89
Westminster—Marylebone Road	121	106	356	329	94	94
Inner London–Roadside						
Camden—Swiss Cottage	n.a.[g]	n.a.[h]	n.a.[g]	n.a.[h]	46[g]	35[h]
K & C—Cromwell Road	64	59	188	184	96	94
K & C—Kings Road	87	78	266	239	96	89
K & C—Knightsbridge	78	72	298	291	96	97
Lewisham—New Cross	n.a.[i]	45	n.a.[i]	165	43[i]	98
Southwark—Old Kent Road	52	43	182	156	88	93
Tower Hamlets—Mile End Road	72	54	239	194	93	95
Wandsworth—High Street	31	27	171	145	96	95
Inner London–Urban Background						
Islington—Upper Street	17	16	117	106	96	94
K & C—North Kensington	15	14	113	104	96	93
K & C—Pembroke Road	18	17	107	102	97	96
Southwark—Elephant and Castle	25	21	111	101	83	86
Tower Hamlets—Poplar	13	12	101	98	95	94
Tower Hamlets—Bethnal Green	17	14	111	96	92	76
Suburban Outer London						
Bexley—Slade Green	13	14	101	115	93	91
Brent—Kingsbury	12	12	108	116	96	93
Greenwich—Eltham	10	10	84	81	96	95
Mole Valley—Lower Ashstead	9	8	84	75	96	97
Richmond-upon-Thames—Teddington	8	7	78	73	96	93
Suburban Composite	10	10	—	—	100	100

[a] Values are based on hourly mean concentrations. Where capture rate was < 75% for either the before or after period, n.a. (not acquired) and a footnote describe major periods of data loss.

[b] Site reopened April 2003 after a 3-year closure.

[c] Data excluded March 2002 to April 2003 due to a minor leak in the analyzer's NO_x/NO channel switching valve.

[d] Site opened October 2002.

[e] Site opened July 2001.

[f] Site reopened November 2002 after a 2-year closure.

[g] Data excluded February 2002 to May 2004 due to baseline clipping of NO_x channel (dual chamber analyzer).

[h] Data excluded February 2002 to May 2004 due to blocked ozone orifice.

[i] Site opened April 2002.

Table 16. Summary Statistics for NO_2 Measurements for the 2 Years Before and After the CCS Started[a]

	Mean (ppb)		98th Percentile (ppb)		Capture Rate (%)	
Monitoring Site	Pre	Post	Pre	Post	Pre	Post
Within CCZ–Roadside						
Camden—Shaftesbury Avenue	37.0	37.2	69	69	97	94
Westminster—Victoria Street	n.a.[b]	17.8	n.a.[b]	36	0[b]	68
Within CCZ–Urban Background						
Bloomsbury—Russell Square	n.a.[c]	30.2	n.a.[c]	55	43[c]	87
City of London—Senator House	n.a.[d]	28.1	n.a.[d]	55	62[d]	84
Westminster—Horseferry Road	n.a.[e]	n.a.	n.a.[e]	n.a.	71[e]	77
IRR–CCZ Boundary						
Hackney— Old Street	n.a.[f]	32.4	n.a.[f]	61	12[f]	89
Westminster—Marylebone Road	43.1	57.6	84	123	94	94
Inner London–Roadside						
Camden—Swiss Cottage	n.a.[g]	n.a.[h]	n.a.[g]	n.a.[h]	46[g]	35[h]
K & C—Cromwell Road	38.6	40.7	70	75	96	94
K & C—Knightsbridge	44.2	47.3	100	111	96	97
K & C—King's Road	44.3	50.0	78	94	96	89
Lewisham—New Cross	n.a.[i]	34.7	n.a.[i]	76	43[i]	98
Southwark—Old Kent Road	32.3	33.6	56	61	88	81
Tower Hamlets—Mile End Road	34.5	33.1	68	67	93	95
Wandsworth—High Street	25.0	25.9	59	65	95	95
Inner London–Urban Background						
Islington—Upper Street	24.3	24.7	49	53	96	93
K & C—North Kensington	21.1	21.8	48	53	96	93
K & C—Pembroke Road	25.2	27.5	49	59	97	96
Southwark—Elephant and Castle	26.1	26.0	50	52	83	86
Tower Hamlets—Poplar	21.9	20.0	46	48	95	94
Tower Hamlets—Bethnal Green	23.6	22.4	48	48	92	76
Suburban Outer London						
Bexley—Slade Green	17.4	18.6	41	46	92	91
Brent—Kingsbury	17.0	16.3	43	47	96	93
Greenwich—Eltham	16.3	17.6	41	46	96	95
Mole Valley—Lower Ashstead	13.9	13.6	34	35	96	97
Richmond-upon-Thames—Teddington	14.0	13.6	39	40	96	93
Suburban Composite	15.7	15.9	—	—	100	100

[a] Values are based on hourly mean concentrations. Where capture rate was < 75% for either the before or after period, n.a. (not acquired) and a footnote describe major periods of data loss.

[b] Site reopened April 2003 after a 3-year closure.

[c] Data excluded March 2002 through April 2003 due to a minor leak in the analyzer's NO_x/NO channel switching valve.

[d] Site opened October 2002.

[e] Site opened July 2001.

[f] Site reopened November 2002 after a 2-year closure.

[g] Data excluded February 2002 to July 2003 due to baseline clipping of NO_x channel (dual chamber analyzer).

[h] Data excluded January 2004 to May 2004 due to blocked ozone orifice.

[i] Site opened April 2002.

The pattern of decreasing NO concentrations at Inner London sites was not repeated for NO_2 (Table 16). The changes at Inner London–Urban Background sites were similar to those of suburban sites, with increases and decreases of less than 10%. All but two roadside sites also showed little change: K & C—King's Road (Inner London–Roadside) and Westminster—Marylebone Road (IRR–CCZ Boundary) recorded increases in mean NO_2 of 13% and 34%, respectively. These increases in NO_2 equated to the decreases in NO at these sites resulting in no overall change in NO_x concentrations (Table 14). NO_x concentrations at Camden—Shaftesbury Avenue (Within CCZ–Roadside) decreased by 8%, reflecting a decrease in NO with little change in NO_2.

Mean PM_{10} concentrations at all sites were higher during the 2 years after the CCS was introduced than during the 2 years before (Table 17). This increase was due,

Table 17. Summary Statistics for PM_{10} Measurements for the 2 Years Before and After the CCS Started[a]

	Mean (µg/m³)		98th Percentile (µg/m³)		Capture Rate (%)	
Monitoring Site	Pre	Post	Pre	Post	Pre	Post
Within CCZ–Roadside						
Camden—Shaftesbury Avenue	26.6	28.3	57	66	98	98
Within CCZ–Urban Background						
Bloomsbury—Russell Square	n.a.[b]	21.1	n.a.[b]	48	60[b]	84
IRR–CCZ Boundary						
Hackney—Old Street	n.a.[c]	26.8	n.a.[c]	62	9[c]	84
Westminster—Marylebone Road	33.4	34.9	72	76	94	99
Inner London–Roadside						
Camden—Swiss Cottage	24.1	27.1	55	64	99	97
K & C—Cromwell Road	27.4	28.1	58	61	96	95
Lewisham—New Cross	n.a.[d]	25.5	n.a.[d]	64	33[d]	93
Southwark—Old Kent Road	n.a.[e]	26.8	n.a.[e]	67	62[e]	76
Wandsworth—High Street	20.9	23.1	53	61	98	96
Inner London–Urban Background						
Islington—Upper Street	19.7	21.2	48	54	99	97
K & C— North Kensington	19.1	20.2	47	53	98	97
Southwark—Elephant and Castle	n.a.[f]	21.9	n.a.[f]	54	15[f]	93
Tower Hamlets—Poplar	18.7	21.5	47	59	97	96
Tower Hamlets—Bethnal Green	20.4	20.8	50	52	92	88
Suburban Outer London						
Bexley—Slade Green	18.5	19.6	51	54	97	94
Brent—Kingsbury	17.9	18.3	44	50	98	95
Greenwich—Eltham	17.6	19.2	42	52	96	94
Mole Valley—Lower Ashstead	16.6	17.0	40	44	98	99
Suburban Composite	17.7	18.4	—	—	100	100

[a] Values are based on hourly mean concentrations. PM_{10} was measured with TEOMs at these sites. Where capture rate was < 75% for either the before or after period, n.a. (not acquired) and a footnote describe major periods of data loss.

[b] Extended TEOM fault led to exclusion of data between June 2002 and May 2003.

[c] Site reopened November 2002 after a 2-year closure.

[d] The TEOM was added to the existing site in August 2001; recurring analyzer faults between April and July 2002.

[e] Site opened April 2002.

[f] The TEOM was added to the existing site in October 2002.

Table 18. Summary Statistics for $PM_{2.5}$ Measurements for the 2 Years Before and After the CCS Started[a]

	Mean (µg/m^3)		98th Percentile (µg/m^3)		Capture Rate (%)	
Monitoring Site	Pre	Post	Pre	Post	Pre	Post
Within CCZ–Roadside						
None available	—	—	—	—	—	—
Within CCZ–Urban Background						
Bloomsbury—Russell Square	13.0	13.3	33	35	100	97
IRR–CCZ Boundary						
Westminster—Marylebone Road	n.a.[b]	19.2	n.a.[b]	43	6[b]	94
Inner London–Roadside						
None available	—	—	—	—	—	—
Inner London–Urban Background						
None available	—	—	—	—	—	—
Suburban Outer London						
Bexley—Belvedere	11.2	12.6	31	38	77	98

[a] Values are based on hourly mean concentrations. Where capture rate was < 75% for either the before or after period, n.a. (not acquired) and a footnote describe major periods of data loss.

[b] Data excluded until January 1, 2003, due to TEOM configuration fault.

in part, to an unusually high incidence of easterly winds that imported PM from Continental Europe (Fuller 2005).

$PM_{2.5}$ was monitored at only one station in Suburban Outer London, one at the IRR–CCZ Boundary, and one Within CCZ–Urban Background. Data are in Table 18.

Inner London–Roadside concentrations of CO decreased by 17% to 25% over the 4-year period (Table 19).

Black smoke was monitored in Suburban Outer London (3 sites), on the CCZ boundary (1 roadside site), and within the CCZ (2 background sites). Data are presented in Table 20.

TIME-SERIES CHARTS

The time-series charts in Appendix G show daily mean concentrations of NO, NO_x, NO_2, PM_{10}, $PM_{2.5}$, and CO for the full analysis period, making clear the distribution and nature of missing data for each series. Date-centered running annual means are included on the charts to give an illustration of longer-term trends.

As well as illustrating the distribution of missing data points over the 4-year analysis period, the time-series charts demonstrate the differing influence of meteorology on each indicator site and pollutant. Strong seasonality was evident in the CO, NO, and NO_x measurements at all sites.

PM_{10} concentrations were not as seasonally dependent, but showed clear episodic peaks throughout the period. At many of the sites, the highest peaks occurred in February and in August 2003 just after the CCS was introduced. The exception to this is at Bloomsbury—Russell Square (Within CCZ–Urban Background, Appendix Figure G.6). PM_{10} data from this site between June 2002 and March 2003 were excluded due to an equipment fault. Before this, the site recorded a period of high peak PM_{10} concentrations

Table 19. Summary Statistics for CO Measurements for the 2 Years Before and After the CCS Started[a]

	Mean (ppb)		98th Percentile (ppb)		Capture Rate (%)	
Monitoring Site	Pre	Post	Pre	Post	Pre	Post
Within CCZ–Roadside						
Westminster—Victoria Street	n.a.[b]	0.2	n.a.[b]	0.6	0[b]	85
Within CCZ–Urban Background						
Bloomsbury—Russell Square	0.4	0.3	1.2	0.9	93	93
Westminster—Horseferry Road	0.5	0.4	1.2	1.0	76	92
IRR–CCZ Boundary						
Westminster—Marylebone Road	1.3	1.0	3.7	2.5	95	95
Inner London–Roadside						
K & C—Cromwell Road	0.9	0.7	2.1	1.6	95	92
Southwark—Old Kent Road	0.9	n.a.[c]	2.1	1.5[c]	86	67[c]
Tower Hamlets— Mile End Road	0.5	0.5	1.5	1.1	96	86
Wandsworth—High Street	0.6	0.5	2	1.5	92	95
Inner London–Urban Background						
K & C—North Kensington	0.4	0.4	1.1	1.0	93	94
K & C—Pembroke Road	0.3	0.4	1.3	0.9	97	95
Southwark—Elephant and Castle	0.4	0.4	1.2	1.0	94	94
Suburban Outer London						
Bexley—Slade Green	0.3	0.3	1.0	1.0	93	93
Brent—Kingsbury	0.2	0.2	1.6	1.3	99	84
Suburban Composite	0.2	0.3	—	—	100	91

[a] Values are based on hourly mean concentrations. Where capture rate was < 75% for either the before or after period, n.a. (not acquired) and a footnote describe major periods of data loss.

[b] Site reopened April 2003 after a 3-year closure.

[c] Data lost between April 2003 and October 2003 due to analyzer fault.

between March and May 2002 that were emitted from building works close to the site inlet (Vallance-Plews 2003). Because the analyzer was operating correctly during this period, the data ratification process did not exclude these data. However, this strong local source of PM_{10} throughout much of the pre-CCS period for which we have valid data confounds any assessment of change in PM_{10} concentrations at the Bloomsbury—Russell Square site that might be associated with the CCS. Nevertheless, PM_{10} data from this site were included in the analysis presented in the next section; therefore, those results must be considered in relation to this interference.

The most striking upward change over the time period was seen in NO_2 concentrations at the Westminster—Marylebone Road curbside site on the IRR–CCZ Boundary (Appendix Figure G.12). The smoothed trend line shows a clear increase during 2003, followed by a period of stability at this new higher concentration. The change is clearer in the daily mean data, which show both an increase in concentration and variability. This pattern was not repeated in NO_x concentrations, which suggests a decrease in the NO_x-to-NO_2 ratio. Conversely, a steady downward trend is clear in CO concentrations at the same site over the full 4-year period.

Table 20. Summary Statistics for Black Smoke Measurements for the 2 Years Before and After the CCS Started[a]

	Mean (µg/m^3)		Capture Rate (%)	
Monitoring Site	Pre	Post	Pre	Post
Within CCZ–Roadside				
None available	—	—	—	—
Within CCZ–Urban Background				
City of London—Guildhall	8.9	7.5	85	92
Westminster—Grosvenor	9.2	11.8	58[b]	13[c]
IRR–CCZ Boundary				
Westminster—Marylebone Road	26.6	23.1	88	77
Inner London–Roadside				
None available	—	—	—	—
Inner London–Urban Background				
None available	—	—	—	—
Suburban Outer London				
Enfield—Bush Hill Park	4.9	3.6	83	84
Greenwich—Woolwich	5.4	5.7	76	97
Redbridge—Ilford	8.7	7.0	90	89
Suburban Composite	6.7	5.5	100	100

[a] Values are based on hourly mean concentrations.

[b] Very little valid data up to November 2001.

[c] No data beyond June 2003, reasons not yet available from AURN quality control unit.

ANALYSIS OF TEMPORAL CHANGES IN MEAN MEASURED POLLUTANT CONCENTRATIONS ACROSS LONDON

INTRODUCTION

In this section of the project we developed an analytical approach to assessing temporal changes in air pollutant concentrations from before to after the introduction of the CCS. To guide the development of this approach we formulated a series of hypotheses derived from the results of work undertaken earlier in the project. These hypotheses were:

- The effects of the CCS on air pollutant concentrations would most readily be observed during the hours the scheme was in operation.
- Any effects of the CCS would most likely be observed in pollutants whose main source in London is vehicles (NO, NO_2, NO_x, PM_{10}, and CO).
- The CCS would not have an effect on pollutant concentrations measured some distance from the CCZ (assumed to be 8 km or more from the zone's center).

Hence, our analysis focused upon the hours during which the CCS was in operation (7 AM to 6:30 PM) and upon traffic-related pollutants. A control area was designated incorporating all monitoring sites within Greater London but at least 8 km from the center of the CCZ. Note that the control area approximately corresponds to Outer London, which is bounded on the inside by the North and South Circular Roads at a distance of between 6 and 10 km from the CCZ center (see Figure 16). Data from these control sites were used to evaluate baseline temporal patterns in pollutant concentrations that arose from factors operating over shorter (e.g., meteorology) and longer (e.g., natural vehicle fleet turnover) periods of time (i.e., temporal patterns likely to occur within the CCZ if the CCS had not been introduced).

Data for matching CCH during weekends, when the scheme was not in operation, were also analyzed. Under the assumption that the scheme would not have an effect upon pollutant concentrations on the weekend, one would expect to observe the same temporal changes in pollutant concentrations within the CCZ as in the control area.

To further understand the temporal patterns in air pollution across London as a whole, changes in mean pollutant concentrations after the introduction of the CCS were calculated for all monitoring stations in three areas: within the CCZ, in the area surrounding the zone (from the zone boundary out to 8 km from the CCZ center), and in the control area (more than 8 km from the CCZ center). These analyses would indicate the appropriateness of the a priori definition of the control area as being some distance from the CCZ and give an indication of changes in the area surrounding the zone in addition to those changes identified within the CCZ.

Hence, the analysis for this part of the project was divided into three separate components. First, a comparative (within the CCZ vs. control area) analysis of changes in geometric mean pollutant concentrations on weekdays only during charging hours after introduction of the CCS. Second, the same spatial comparison but using data from weekends only. Third, a descriptive analysis of changes in pollutant concentrations over time for all stations within the CCZ, surrounding the zone, and in the control area.

The CCS Study Database, detailed in the previous section, provided the time series of daily pollutant concentrations for the analysis. Data measured at both roadside and background monitoring sites were analyzed. We hypothesized that measurements made at roadside sites were more likely to be affected by this traffic management scheme. Data from background sites were also included to test this hypothesis, because of their relevance to health studies, and because they provide a more representative picture of urban pollution levels. The data analyzed were collected 2 years before and 2 years after the scheme was introduced to ensure that seasonal influences were balanced in the analyses. Furthermore, this time period accommodated the unusual meteorologic conditions in London that had led to periods of elevated pollution levels in 2003, the year the CCS was introduced.

METHODS

Data Compilation

The compilation of the data used for this analysis was described in the previous section on establishing the CCS database. Daily average concentrations during CCS charging hours for 5 pollutants were extracted from the CCS database for the 4-year period. Data were available from a number of monitoring sites across Greater London (102 sites monitoring NO, NO_2, and NO_x; 87 sites monitoring PM_{10}; and 32 sites monitoring CO). The time series began on February 19, 2001 and ended on the February 16, 2005. Daily average concentrations were calculated only on days with at least 75% of hourly observations available during the CCH; otherwise the day's average value was coded as missing.

Selection of Monitoring Sites

As discussed in previous sections, pollution concentrations in London arise from both local and regional sources and daily measured concentrations are subject to temporal trends. It was clear therefore that any temporal changes in pollutant concentrations observed within the CCZ should be adjusted for general, London-wide, temporal trends. The question of which monitoring sites in London represent the regional trends was subject to considerable debate among the project team. An a priori decision was made to use monitors 8 km or more from the center of the CCZ (the control area) as indicators of regional trends in pollution because we assumed that concentrations at these control sites would not be affected by the implementation of the CCS. Only monitoring sites that provided data for at least 75% of the study days during the 4-year period were selected for analysis.

The three criteria used to select the monitoring sites that would provide data for the analysis were:

1. completeness of data (data for 75% of days within the 4-year period and on those days, 75% of hourly observations),
2. site classification (roadside or background), and
3. distance from the CCZ center (within the CCZ or in the control area).

All other data were excluded from further consideration.

Statistical Methods

Temporal changes were assessed using the change in geometric mean pollutant concentrations measured 2 years before and 2 years after the scheme's introduction. By design, this method removed London-wide temporal factors such as meteorologic conditions and trends in air pollution that could confound the effects of the introduction of the CCS. We achieved this by using the temporal patterns in pollutant concentrations at the control sites as indicators of the patterns across London as a whole and hence across the CCZ. Data processing and analysis were simple and transparent, and the method facilitated testing a number of hypotheses relating to the air pollution changes linked to the CCS.

An initial visual assessment of the air pollutant data was made by plotting the time series of observed values. To aid this assessment, the natural logarithms of the pollutant measurements were taken and their temporal patterns modeled using natural cubic splines with 2 and 12 degrees of freedom. These plots help illustrate the long-term trends and seasonal patterns present in the data.

Temporal changes in the pollutant concentrations were summarized numerically by the geometric means for the 2-year periods before and after the introduction of the scheme together with the percentage of change in the means.

$$\left(\prod_{i=1}^{n} x_i\right)^{1/n} = \sqrt[n]{x_1 x_2 \ldots x_n} = \exp\left(\frac{1}{n}\sum_{i=1}^{n} \ln x_i\right).$$

This summary statistic is an appropriate measure for air pollution concentrations that tend to follow a log-normal distribution.

In order to assess the relative changes in pollutant concentrations after the introduction of the scheme, we conducted a series of pair-wise comparisons between each site within the CCZ and each site in the control area. Specifically, for each available monitor $j = 1 \ldots J$ within the CCZ and monitor $k = 1 \ldots K$ in the control area, we calculated the geometric means and their ratios, using only days on which both monitors provided data (Table 21).

Each controlled ratio provided an estimate of the post/pre-CCS change in a pollutant measured at monitor j within the CCZ allowing for changes that had occurred at monitor k in the control area. For each pair-wise comparison, including only the days for which both monitors provided data eliminated bias due to imbalance in day effects (e.g., due to weather) between monitors. However, it also meant that each pair-wise comparison was based on somewhat different days. Hence the days used in this comparative analysis are not necessarily those used in the initial descriptive assessment of the data described in Tables 14–19.

$Ratio_j$ and $ratio_k$ were estimated using regression models, a justification of which follows.

We denote the average pollutant concentration during CCH on day i at monitor k in the control area as Y_{ik}. We first assume, for monitor k:

$$\ln\left(Y_{ik}\right) = \beta_k ccs_i + \varepsilon_{ik},$$

where ccs_i is a dichotomous indicator variable (0 = before implementation, 1 = after implementation of the CCS); and ε_{ik} is random noise (expectation zero, independently and identically distributed).

Then, $\ln(ratio_k)$ is clearly an unbiased estimate of β_k. $Ratio_k$ can be interpreted as the mean post/pre-CCS change, due for example to changes in vehicle fleet or weather patterns between the two periods.

For monitors within the CCZ, we assume the same model:

$$\ln\left(Y_{ij}\right) = \beta_j ccs_i + \varepsilon_{ij}.$$

Likewise, $\ln(ratio_j)$ is an unbiased estimate of β_j. $Ratio_j$ can be interpreted as the mean post/pre-CCS change, due for example to changes in vehicle fleet or weather patterns between the two periods plus any CCS effect.

With these assumptions,

$$\begin{aligned} controlled\ ratio_{j,k} &= ratio_j \ / \ ratio_k \\ &= \exp\left[\beta_j - \beta_k + \left(\sum_{ccs=1} \varepsilon_{ij} - \sum_{ccs=0} \varepsilon_{ij}\right)\right. \\ &\qquad \left. - \left(\sum_{ccs=1} \varepsilon_{ik} - \sum_{ccs=0} \varepsilon_{ik}\right)\right] \end{aligned}$$

Thus under these assumptions, $\ln(ratio_j / ratio_k)$ is an unbiased estimate of $\beta_j - \beta_k$, and $(ratio_j / ratio_k)$ is a median-unbiased estimate of the change due to introduction of the CCS, on the assumption that other factors would have had the

Table 21. Derivation of Controlled Ratios

	Before CCS Start	After CCS Start	Ratio
Within CCZ	$GM_{j,before}$	$GM_{j,after}$	$ratio_j = GM_{j,after} / GM_{j,before}$
Control area	$GM_{k,before}$	$GM_{k,after}$	$ratio_k = GM_{k,after} / GM_{k,before}$
Controlled ratio			$ratio_{j,k} = ratio_j / ratio_k$

same impact within and outside the zone. This assumption is made more plausible by including in both monitor series only those days for which data were available for both, so that day effects common to both will cancel.

Standard errors of the ratios were estimated under the assumption that each of the deviations (ε) in the expression above are independent (i.e., $\mathrm{SE}[\ln\{\mathrm{GM}\}] = s/\sqrt{n}$). This is an approximation because autocorrelation will generate dependence of deviations. Further, for the controlled ratio, the inclusion of the same days in the two monitor series will induce dependence from day effects common to both series. Thus the uncertainty in $\ln(ratio_j/ratio_k)$ as an estimate of $\beta_j - \beta_k$ is likely to be overestimated. However, given our use of random-effects models to obtain mean controlled ratios over all the contributing monitors, the uncertainty in those means should be correctly stated.

The confidence intervals for this statistic were calculated (and expressed as percentages) as:

$$\exp\left[\beta_j - \beta_k \pm 1.96 \times \sqrt{\mathrm{SE}\left(\beta_j\right)^2 + \mathrm{SE}\left(\beta_k\right)^2}\right].$$

These pair-wise ratios were then graphed in a forest plot, and a mean for each site within the CCZ was estimated by standard random-effects meta-analytical methods (DerSimonian and Laird 1986).

The software package SPLUS was used for all analyses.

RESULTS

Analysis of Weekday Data

Data Description In Appendix H (available on the HEI Web site), Tables H.1 through H.10 give descriptive statistics for all monitoring sites grouped by site classification (within the CCZ or in the control area, and roadside or background). For each pollutant, one table presents descriptive statistics for CCH for the full 4 years, and another table presents the same statistics divided into the years before and after CCS implementation. Sites selected for analysis based upon data completeness, site classification, and distance from the CCZ center are shaded.

Time-series plots of daily mean concentrations for each pollutant together with smoothers to illustrate temporal trends and seasonal patterns are given in Figures H.1 through H.9. Here tables give data for monitors Within CCZ–Roadside and Within CCZ–Urban Background.

Site Selection For NO, NO_2, and NO_x, only 1 roadside monitoring site (Camden—Shaftesbury Avenue) and 3 background sites (Bloomsbury—Russell Square; City of London—Senator House; and Westminster—Horseferry Road) within the CCZ provided NO data for analysis. NO concentrations from monitors in the control area were available for 16 roadside and 7 background sites. Data from the Bromley—Harwood Avenue site were excluded from the analyses due to a change in the sampling inlet location during the monitoring period.

For PM_{10}, one roadside monitoring site (Camden—Shaftesbury Avenue) and one background site (Bloomsbury—Russell Square) within the CCZ provided data for analysis; PM_{10} concentrations in the control area were available from 14 roadside and 5 background monitoring sites.

CO was not monitored at any roadside sites within the CCZ during the analysis period. Background monitoring sites within the CCZ at Bloomsbury—Russell Square and Westminster—Horseferry Road provided data for this analysis. In addition, a single control site (Enfield—Salisbury School) had sufficient data for analysis.

Data Availability Tables H.11 through H.14 list the number of days with data available for analyses in each pair-wise comparison for each pollutant (except CO).

Analysis of Geometric Means Key results for each pollutant studied (NO_x, NO, NO_2, PM_{10}, and CO) are presented in Tables 22 through 25. The results shown in Tables 22 and 23 are also shown graphically in Figure 18. Table 24 shows results for background sites during the weekends (see the section Analysis of Weekend Data). Random-effects summary estimates of controlled ratios for roadside and background sites are shown in Table 25 for weekdays and weekends. These results show percent changes in concentrations within the CCZ compared with those in the control area. The full results are presented in Appendix I (available on the HEI Web site) with a series of tables and figures that illustrate the controlled ratios calculated for each pollutant and monitoring station.

Summary of Findings from the Weekday Analysis Changes in geometric mean concentrations of NO, NO_x, NO_2, and PM_{10} recorded during weekday CCH at roadside sites within the CCZ and in the control area are shown in Table 22. Equivalent results for background sites are shown in Table 23 (with the addition of CO results).

Analysis of Weekday Data from Roadside Sites

- NO_x levels measured at Camden—Shaftesbury Avenue (within the CCZ) fell by 5.0% after the introduction of the CCS. However, NO_x levels also fell at 12 of 16 sites in the control area (range 19.3% to 1.4%). NO_x concentrations increased at 4 of 16 sites (2.7% to 17.2%) (Table 22).

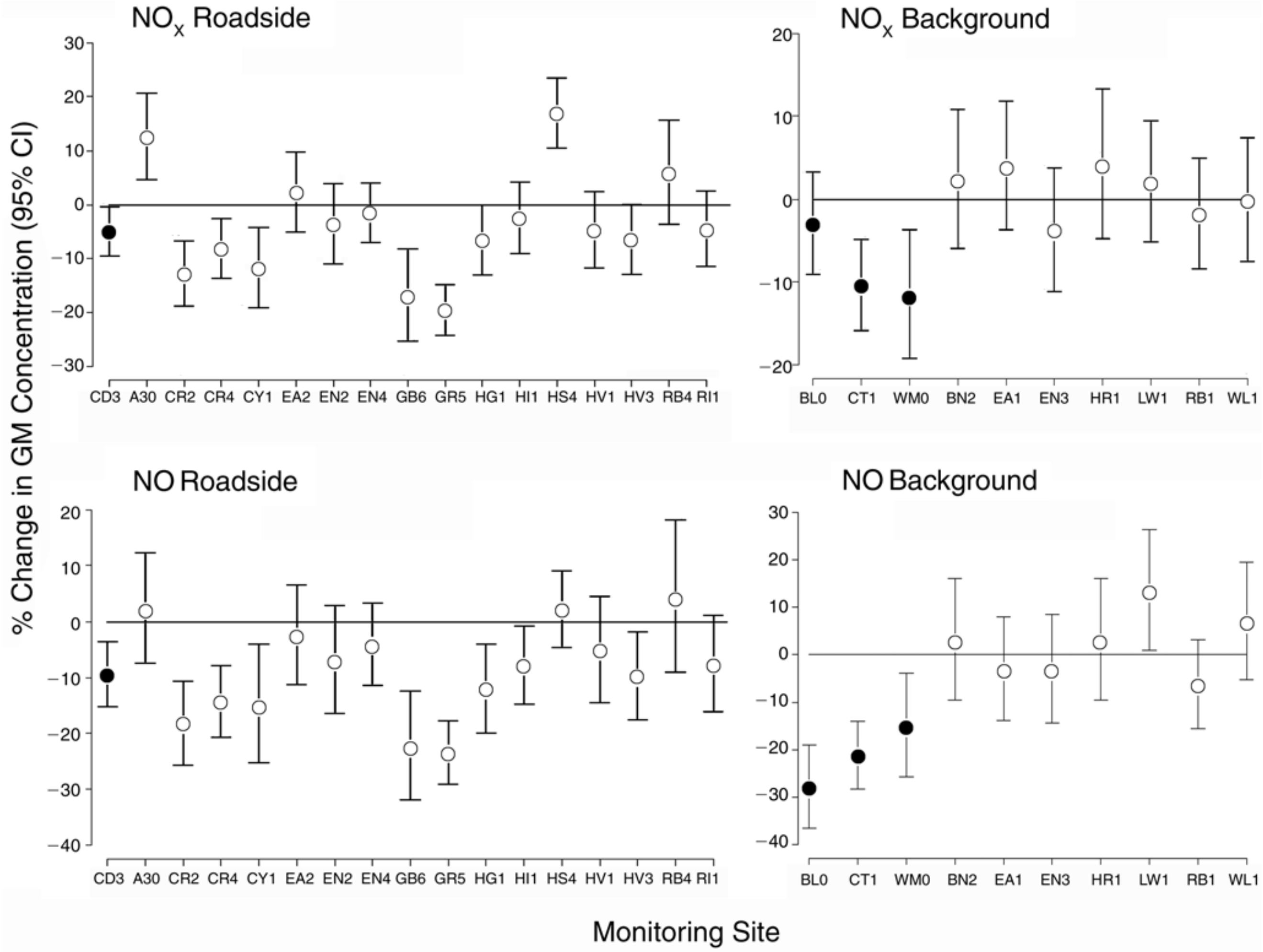


Figure 18. Percent changes in GM concentrations of NO$_x$, NO, NO$_2$, and PM$_{10}$ (next page) on weekdays before and after CCS introduction at roadside and background locations stratified by station location (within the CCZ [filled circles] **and outside the zone** [in the control area; at least 8 km from the center of the CCZ and within Greater London; open circles]**) and plotted according to the site's distance from the CCZ center.** (See Tables 22 and 23 for monitoring site codes.)

- NO levels measured at Camden—Shaftesbury Avenue fell by 9.6% after the introduction of the CCS. They also fell at 13 of 16 sites in the control area (23.1% to 2.0%) and rose at 3 of 16 sites (2.2% to 4.5%) (Table 22).
- NO$_2$ levels measured at Camden—Shaftesbury Avenue increased by 1.9% after the introduction of the CCS. In the control area, NO$_2$ levels decreased at 7 of 16 sites (14.4% to 0.7%) and increased at 9 of 16 sites (0.6% to 44.7%) (Table 22).
- Changes in NO$_x$, NO, and NO$_2$ levels measured at Camden—Shaftesbury Avenue were, on average, 0.9%, 0.4%, and 2.2% lower, respectively, compared with changes at the 16 locations in the control area (random-effects summary estimates of controlled ratios; Table 25). In each set of comparisons, strong evidence of heterogeneity in the estimated relative changes was apparent.
- PM$_{10}$ concentrations measured at Camden—Shaftesbury Avenue increased by 5.7% after the introduction of the CCS. In the control area, PM$_{10}$ concentrations decreased at 5 of 14 sites (0.5% to 11.0%) and increased at 9 of 14 sites (0.9% to 15.4%) (Table 22).
- Changes in PM$_{10}$ concentrations measured at Camden—Shaftesbury Avenue were, on average, 2.3% higher compared with changes at the 14 locations in the control area (Table 25). Strong evidence of heterogeneity in the estimated relative changes was apparent.

Analysis of Weekday Data from Background Sites

- NO$_x$ levels measured at the 3 stations within the CCZ fell by 3.1%, 10.2%, and 11.8% compared with no change at 1 site in the control area, falls of 3.7% and 1.7% at 2 of 7 control sites, and rises of between 2.4% and 4.4% at 4 of 7 control sites (Table 23). Changes in

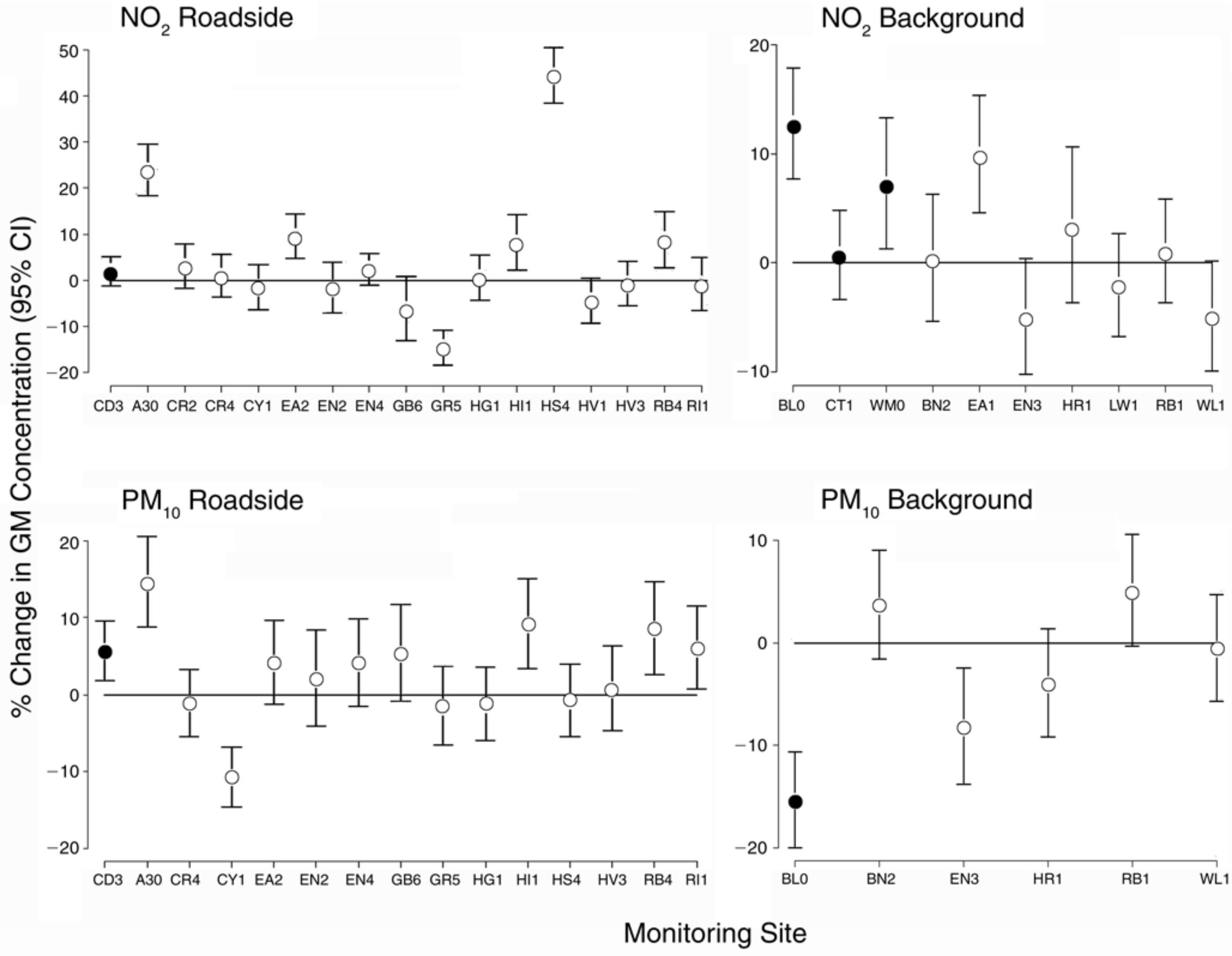


Figure 18 (*Continued*).

NO$_x$ levels measured at the 3 locations in the CCZ were, on average, −2.7%, −4.4%, and +1.2% compared with changes at the 7 background locations in the control area (Table 25).

- NO levels fell by 28.3%, 21.0%, and 14.6% at the 3 stations within the CCZ compared with falls of between 2.7% and 6.3% at 3 of 7 control sites and rises of between 3.0% and 13.8% at 4 of 7 control sites (Table 23). Changes in NO levels measured at 3 locations in the CCZ were, on average, 25.0%, 10.5%, and 12.3% lower than changes at the 7 background locations in the control area (Table 25).
- NO$_2$ levels increased by 0.9%, 7.4%, and 12.7% at the 3 stations within the CCZ compared with falls of between 1.8% and 5.0% at 3 of 7 control sites and rises of between 0.6% and 10.3% at 4 of 7 control sites (Table 23). Changes in NO$_2$ levels measured at 3 locations in the CCZ were, on average, 20.2%, 2.1%, and 8.8% higher than changes at the 7 background locations in the control area (Table 25).
- PM$_{10}$ concentrations at Bloomsbury—Russell Square (within the CCZ) fell by 15.4% after CCS implementation compared with smaller decreases of 0.5% to 8.0% at 3 of 5 control sites and rises of 3.7% and 5.2% at 2 of 5 control sites (Table 23). Changes in PM$_{10}$ concentrations measured at Bloomsbury—Russell Square were, on average, 12.4% lower than changes at the 5 background locations in the control area (Table 25).
- CO concentrations fell by 22.5% and 25.4% at the two monitoring sites within the CCZ. At the one monitor in the control area, CO concentrations fell by 2.3% after the introduction of the CCS (Table 23).

Table 22. Differences in GM Concentrations Before and After CCS Introduction at Roadside Locations Within and Outside the Zone for Weekdays[a]

		NO_x (ppb)			NO (ppb)			NO_2 (ppb)			PM_{10}[b] (µg/m^3)		
Monitoring Site	Code	GM Pre	GM Post	% Change	GM Pre	GM Post	% Change	GM Pre	GM Post	% Change	GM Pre	GM Post	% Change
Within the CCZ													
Camden—Shaftesbury Avenue	CD3	107.6	102.2	−5.0	63.9	57.8	−9.6	42.1	43.0	1.9	41.0	43.3	5.7
Outside the Zone[c]													
Croydon—Purley Way	CR2	105.2	91.0	−13.5	72.6	58.6	−19.3	29.0	29.9	2.9	—	—	—
Croydon—George Street	CR4	73.6	67.8	−7.9	41.3	35.5	−14.0	31.2	31.5	1.1	32.6	32.3	−1.0
Crystal Palace—Crystal Palace Parade	CY1	78.7	69.0	−12.4	45.6	38.3	−16.1	28.0	27.5	−1.6	32.8	29.2	−11.0
Ealing—Acton Town Hall	EA2	88.3	90.7	2.7	55.6	54.5	−2.0	30.6	33.6	9.8	31.8	33.3	4.7
Enfield—Church Street	EN2	46.1	44.7	−3.1	21.5	20.1	−6.4	23.5	23.2	−1.2	28.3	28.9	2.4
Enfield—Derby Road Upper Edmonton	EN4	74.4	73.3	−1.4	41.9	40.2	−4.0	30.7	31.4	2.4	38.9	40.7	4.5
Greenwich Bexley—Falconwood	GB6	86.8	72.5	−16.5	57.3	44.7	−22.1	27.2	25.6	−5.9	29.9	31.7	5.9
Greenwich—Trafalgar Road	GR5	76.0	61.4	−19.3	42.3	32.6	−23.1	32.4	27.8	−14.4	29.5	29.1	−1.2
Haringey—Town Hall	HG1	57.4	53.7	−6.5	31.2	27.5	−12.0	24.8	24.9	0.6	28.1	27.7	−1.2
Hillingdon—South Ruislip	HI1	76.2	74.5	−2.2	51.1	47.2	−7.6	24.3	26.4	8.3	28.9	31.5	9.2
Hounslow—Chiswick High Road	HS4	98.8	115.9	17.2	64.6	66.2	2.4	33.4	48.4	44.7	35.6	35.5	−0.5
Havering—Rainham	HV1	56.4	53.5	−5.2	30.0	28.2	−5.8	24.7	23.5	−4.6	—	—	—
Havering—Romford	HV3	60.7	56.7	−6.6	36.2	32.6	−10.1	23.1	22.9	−0.9	27.7	27.9	0.9
Redbridge—Gardner Close	RB4	57.4	60.9	6.2	29.0	30.3	4.5	25.4	27.7	9.0	28.7	31.2	8.8
Richmond—Castelnau	RI1	47.9	45.8	−4.4	23.5	21.7	−7.7	23.2	23.1	−0.7	26.3	28.0	6.1
Wandsworth—A3	A30	108.6	118.6	9.3	70.2	71.8	2.2	34.4	42.6	24.0	29.3	33.7	15.0

[a] Data for CCH only; percent change in GM concentration from before to after the introduction of the CCS. No CO data available from roadside locations.

[b] — indicates data not available.

[c] Outside the zone (control area) is beyond 8 km from the CCZ center and within Greater London.

Analysis of Weekend Data

Data Description Data for matching CCH (7:00 AM to 6:30 PM) on Saturdays and Sundays were extracted from the CCS database. The series covering the same 4-year period as in the weekday analysis began on Saturday, February 17, 2001, and ended on Sunday, February 13, 2005, comprising 418 days. The pollutants and the monitoring sites were the same as those selected for the weekday analyses but were restricted to background monitoring stations only. Appendix J (Tables J.1 through J.10; available on the HEI Web site) gives summary statistics for the five pollutants for weekend hours for the background monitoring

Table 23. Differences in GM Concentrations Before and After CCS Introduction at Background Locations Within and Outside the Zone for Weekdays[a]

		NO_x (ppb)			NO (ppb)			NO_2 (ppb)			PM_{10}[b] (μg/m^3)			CO[b] (ppb)		
Monitoring Site	Code	GM Pre	GM Post	% Change	GM Pre	GM Post	% Change	GM Pre	GM Post	% Change	GM Pre	GM Post	% Change	GM Pre	GM Post	% Change
Within CCZ																
Bloomsbury—Russell Square	BL0	60.2	58.3	−3.1	32.6	23.4	−28.3	29.0	32.7	12.7	35.6	30.1	−15.4	0.42	0.33	−22.5
City of London—Senator House	CT1	62.7	56.3	−10.2	30.4	24.0	−21.0	30.5	30.8	0.9	—	—	—	—	—	—
Westminster—Horseferry Road	WM0	49.1	43.3	−11.8	21.9	18.7	−14.6	25.1	26.9	7.4	—	—	—	0.48	0.35	−25.4
Outside the Zone[c]																
Barnet—Finchley	BN2	28.1	28.8	2.5	9.0	9.3	3.0	17.9	18.1	0.6	23.1	24.0	3.7	—	—	—
Ealing—Ealing Town Hall	EA1	35.7	37.2	4.4	14.3	13.9	−2.7	19.6	21.6	10.3	—	—	—	—	—	—
Enfield—Salisbury School	EN3	26.2	25.2	−3.7	8.4	8.1	−3.2	16.7	15.8	−5.0	23.3	21.5	−8.0	0.36	0.35	−2.3
Harrow—Stanmore	HR1	20.2	21.0	4.3	6.3	6.5	3.3	13.0	13.5	3.4	21.6	20.8	−3.9	—	—	—
Lewisham—Catford	LW1	56.7	58.0	2.4	24.5	27.9	13.8	28.8	28.2	−1.8	—	—	—	—	—	—
Redbridge—Perth Terrace	RB1	33.9	33.3	−1.7	13.0	12.2	−6.3	19.8	20.0	1.1	25.0	26.3	5.2	—	—	—
Waltham Forest—Dawlish Road	WL1	30.6	30.6	0.0	9.8	10.5	7.2	19.8	18.8	−4.9	24.5	24.3	−0.5	—	—	—

[a] Data for CCH only; percent change in GM concentration from before to after the introduction of the CCS.

[b] — indicates data not available.

[c] Outside the zone (control area) is beyond 8 km from the CCZ center and within Greater London.

Table 24. Differences in GM Concentrations Before and After CCS Introduction at Background Locations Within and Outside the Zone for Weekend Matching CCH[a]

Monitoring Site	NO_x (ppb)			NO (ppb)			NO_2 (ppb)			PM_{10}[b] (µg/m^3)			CO[b] (ppb)		
	GM Pre	GM Post	% Change	GM Pre	GM Post	% Change	GM Pre	GM Post	% Change	GM Pre	GM Post	% Change	GM Pre	GM Post	% Change
Within CCZ															
Bloomsbury—Russell Square	39.3	39.1	−0.4	19.8	13.1	−34.1	21.8	24.5	12.5	26.9	23.3	−13.4	0.32	0.28	−11.6
City of London—Senator House	35.8	30.8	−14.0	13.1	9.4	−28.3	21.3	20.4	−3.9	—	—	—	—	—	—
Westminster—Horseferry Road	26.3	27.0	2.6	0.0	0.0	−21.1	16.2	18.2	12.8	—	—	—	0.40	0.30	−26.2
Outside the Zone[c]															
Barnet—Finchley	17.7	17.7	0.4	4.7	4.6	−2.7	12.2	12.5	2.0	19.1	19.5	2.4	—	—	—
Ealing—Ealing Town Hall	23.9	21.7	−9.0	8.1	6.0	−26.5	14.4	14.8	2.6	—	—	—			
Enfield—Salisbury School	17.2	15.6	−9.2	4.7	4.1	−12.9	11.8	11.0	−6.4	20.1	18.2	−9.8	0.32	0.30	−3.8
Harrow—Stanmore	13.2	13.0	−1.7	3.8	3.5	−7.5	9.0	9.0	0.4	17.8	17.3	−2.5	—	—	—
Lewisham—Catford	37.4	35.7	−4.6	13.8	14.8	6.8	21.1	19.7	−6.4	—	—	—	—	—	—
Redbridge—Perth Terrace	21.4	20.4	−4.8	6.8	5.9	−12.9	13.9	13.9	−0.3	22.1	23.3	5.6	—	—	—
Waltham Forest—Dawlish Road	20.1	18.8	−6.2	0.0	5.3	4.2	13.9	12.8	−8.0	20.1	21.0	4.6	—	—	—

[a] Percent change in GM concentration from before to after the introduction of the CCS.

[b] — indicates data not available.

[c] Outside the zone (control area) is beyond 8 km from CCZ center and within Greater London.

Table 25. Random-Effects Summary Estimates of Controlled Ratios: Results for CCH for Weekdays and Weekends at Roadside and Background Sites[a]

	Roadside		Background					
	Camden— Shaftesbury Avenue		Bloomsbury— Russell Square		City of London— Senator House		Westminster— Horseferry Road	
Pollutant	Estimate	95% CI	Estimate	95% CI	Estimate	95% CI	Estimate	95% CI
NO_x								
Weekdays	−0.9	−5.3 to 3.8	−2.7	−6.5 to 1.3	−4.4	−8.4 to −0.2	1.2	−3.3 to 5.9
Weekends	−2.6	−7.5 to 2.7	5.6	−1.4 to 13.1	1.9	−5.5 to 9.9	16.3	7.0 to 26.3
NO								
Weekdays	−0.4	−4.7 to 4.1	−25.0	−34.5 to −14.2	−10.5	−16.0 to −4.7	−12.3	−18.3 to −5.9
Weekends	−3.7	−8.5 to 1.5	−21.3	−32.6 to −8.3	−5.1	−15.2 to 6.1	−0.4	−14.9 to 16.5
NO_2								
Weekdays	−2.2	−7.8 to 3.6	20.2	14.0 to 26.8	2.1	−2.1 to 6.6	8.8	4.0 to 13.8
Weekends	−4.2	−9.9 to 1.9	26.0	18.5 to 34.0	5.5	−0.4 to 11.7	−0.1	12.7 to 27.9
PM_{10}								
Weekdays	2.3	−0.9 to 5.6	−12.4	−16.3 to −8.4				
Weekends	4.7	1.6 to 7.8	−10.3	−15.7 to −4.4				

[a] Values are mean net results of percent changes within the CCZ compared with the control area. See Table 21 and accompanying text for discussion of controlled ratios.

sites used in the analysis and lists the number of days available for analysis in each pair-wise comparison for each pollutant (Tables J.11 through J.14). Time-series plots are shown in Figures J.1 through J.5.

The results of the weekend analysis of geometric means before and after implementation of the CCS are summarized in Table 24 for individual sites and Table 25 for the controlled ratio analysis. Full details are given in Appendix K (available on the HEI Web site).

Summary of Findings from the Weekend Analysis

Analysis of Weekend Data from Background Sites

- NO_x levels changed by −0.4%, −14.0%, and +2.6% at the 3 stations within the CCZ compared with falls between 1.7% and 9.2% at 6 of 7 sites in the control area and a rise of 0.4% at the remaining control site (Table 24). NO_x concentrations increased at 3 locations in the CCZ by, on average, 5.6%, 1.9%, and 16.3% compared with changes at the 7 background locations in the control area (Table 25).
- NO levels fell by 34.1%, 28.3%, and 21.1% at the 3 stations within the CCZ compared with falls between 2.7% and 26.5% at 5 of 7 sites in the control area and rises of 4.2% and 6.8% at 2 of 7 control sites (Table 24). NO levels decreased at 3 locations in the CCZ by, on average, 21.3%, 5.1%, and 0.4% compared with changes at the 7 background locations in the control area (Table 25).
- NO_2 levels changed by +12.5%, −3.9%, and +12.8% at the 3 stations within the CCZ compared with falls between 0.3% and 8.0% at 4 of 7 sites in the control area and rises between 0.4% and 2.6% at 3 of 7 control sites (Table 24). Changes in NO_2 levels measured at 3 locations in the CCZ were, on average, 26.0%, 5.5%, and 20.1% higher than changes at the 7 background locations in the control area (Table 25).
- PM_{10} concentrations decreased by 13.4% at the 1 station within the CCZ compared with falls of 2.5% and 9.8% at 2 of 5 sites and small rises between 2.4% and 5.6% at 3 of 5 sites in the control area (Table 24). Changes in PM_{10} concentrations measured at the 1 location in the CCZ were, on average, 10.3% lower than the changes observed at the 5 background locations in the control area (Table 25).
- CO concentrations at the 2 sites within the CCZ fell by 11.6% and 26.2% compared with a smaller decrease of 3.8% observed at the 1 control site (3.8%) (Table 24).

Descriptive Analysis of Changes in Pollutant Concentrations over Time for All Monitoring Sites Within the CCZ, in the Area Surrounding It, and in the Control Area

In the analyses described above, temporal changes in pollutant concentrations measured at monitoring sites within the CCZ were compared with data collected in the control area (defined, a priori, as 8 km or more from the center of the CCZ and within Greater London). That approach left unused the data from a number of monitoring sites in the area surrounding the zone (between the boundary of the CCZ and 8 km from its center; see Figure 16). To assess changes in geometric mean pollutant concentrations across London as a whole, taking into account these previously unused data, a descriptive analysis of data from each background site was carried out to evaluate whether the greater-than-expected falls observed in background concentrations within the CCZ may also have occurred elsewhere. Figure 19 shows the percent changes in geometric mean concentrations as detailed in Tables 22 and 23 ordered according to the distance from the center of the CCZ for weekday data.

These descriptive analyses suggest that the weekday changes in NO and NO_x concentrations before and after CCS introduction were not limited to the CCZ itself. Figure 19 indicates that the magnitude of the percent changes in the concentrations of these two pollutants after the scheme's introduction gradually declines as the distance from the zone center to the monitoring site increases. It was less easy to discern any meaningful pattern for PM_{10} and CO, partly due to the limited availability of data from background sites for these pollutants.

On the weekends, NO levels fell by comparable amounts within the CCZ and in the surrounding area, whereas NO_x levels fell across London generally. NO_2 levels were generally unchanged. Both PM_{10} and CO concentrations on weekends appeared to have changed little over time surrounding the zone and in the control area compared with the clear decreases within the CCZ.

DISCUSSION

The work undertaken in this section of the project involved designing and applying a method to assess the effects of the introduction of the CCS upon pollutant concentrations in London. Specifically, changes in geometric mean pollutant concentrations measured at monitoring sites within the CCZ were compared with changes measured at a number of monitoring sites in the control area. Analyses focused on the five traffic-related pollutants (NO, NO_2, NO_x, PM_{10}, and CO) measured at roadside and background locations on weekdays and weekends.

Summary of Findings from the Weekday Analysis

We found little evidence to support the initial hypothesis that concentrations of roadside pollutants (NO, NO_2, NO_x, and PM_{10}) measured at the single site within the CCZ (i.e., Camden—Shaftesbury Avenue) fell after the introduction of the CCS compared with concentrations measured at sites in the control area. For NO_x, NO, and NO_2 the summary effect estimates (of the relative changes in geometric means) were all negative but imprecisely estimated and all 95% CIs contained zero. For PM_{10}, the summary effect estimate was positive. Furthermore, there was strong evidence for heterogeneity in each set of pair-wise (within the CCZ vs. control area) pollutant comparisons. This finding is contrary to our assumption that the control sites would indicate the overall trend in pollutant concentrations across London as a whole. Indeed, there was no consistency across London in the temporal patterns in roadside pollution concentrations over the 4 years studied.

For some pollutants, however, we saw a clear indication that concentrations measured at background monitoring sites within the CCZ changed more after the introduction of the CCS than those in the control area; the direction of the change depended upon the pollutant measured. Changes in NO_x concentrations, measured at 2 of 3 Within CCZ–Urban Background monitoring sites, were, on average, comparable to changes measured at the 7 sites in the control area. However, some evidence suggested that the composition of NO_x may have changed after the introduction of the CCS. At all 3 background monitoring sites within the CCZ, levels of NO fell compared with changes measured at the control sites, whereas levels of NO_2 increased compared with changes at the control sites. On the whole, the sets of pair-wise comparisons were homogeneous. This was an important finding given that the underlying method relies upon the control sites to indicate London-wide temporal patterns in pollutant concentrations. These patterns of changes in NO_x and its constituents after the introduction of the CCS are consistent with a change in vehicle mix that arose from introducing the CCS. Whereas the number of cars entering the zone is known to have fallen, the number of taxis and buses has increased (TfL 2006). Furthermore, retrofitting particle traps to the bus fleet in London has led to an increase in NO_2 emissions (Air Quality Expert Group [AQEG] 2007).

PM_{10} concentrations measured at a single background location within the CCZ fell, on average, by approximately 12% compared with changes measured at 14 sites in the control area.

The availability of CO data was very limited; only two background sites within the CCZ and one in the control area provided sufficient data for inclusion in the analysis. However, those results that were obtained indicated a relative reduction in CO concentrations.

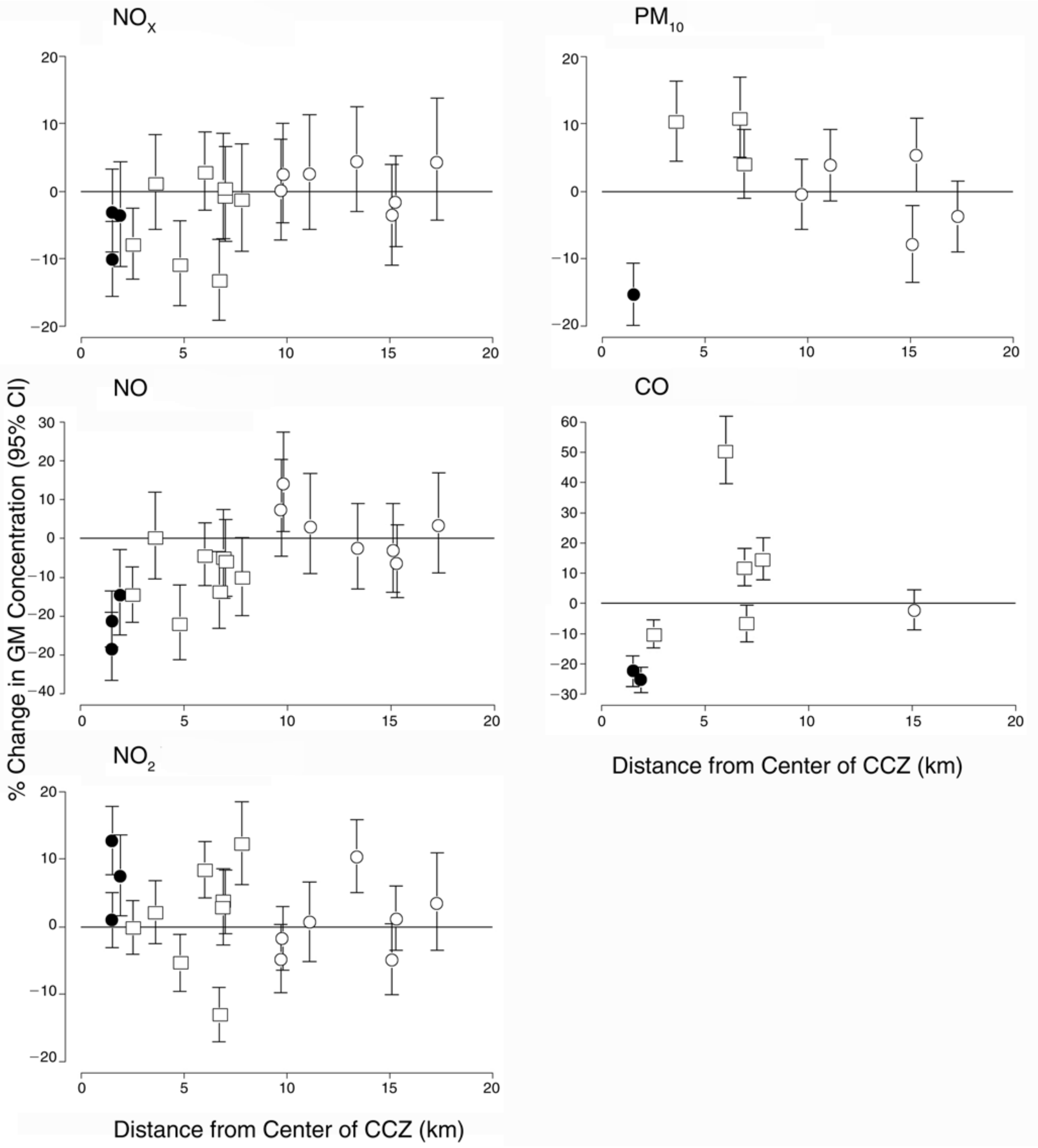


Figure 19. Percent changes in GM concentrations of NO$_X$, NO, NO$_2$, PM$_{10}$, and CO on weekdays before and after CCS introduction at background monitoring stations stratified by station location (within the CCZ [filled circles]**, surrounding the zone** [between the boundary of the CCZ and the inner boundary of the control area; open squares]**, and in the control area** [at least 8 km from the center of the CCZ and within Greater London; open circles]) **and plotted according to the site's distance from the CCZ center.**

Summary of Findings from the Weekend Analysis

The purpose of this additional analysis was to provide a further control for the main weekday analysis. That is, by investigating data that should be free from any effects of the CCS and yet subject to the same temporal and seasonal confounders present in the main analysis, we could better evaluate the findings from the weekday analysis and either accept or reject the hypothesis that implementing the CCS affected some air pollutant concentrations.

If the CCS was indeed responsible for the greater-than-expected falls in background NO and PM_{10} concentrations observed within the CCZ (compared with the control area) during the CCS hours of operation on weekdays, then one would not expect to see any greater or smaller change in pollution other than what would be expected during weekends when the CCS was not in operation. This assumption was based upon the premise that the effects of the CCS were limited to its hours of operation.

For NO, the results from the analysis of Bloomsbury—Russell Square data strongly suggest that falls in concentrations on weekends were comparable to falls observed during the week. For the other two background sites within the CCZ, the weekend data suggest that the temporal patterns in pollution were comparable with those in the control area. For NO_2, relative changes in weekday concentrations were also observed in weekend data. For NO_x data, however, the pattern of results for the 3 background sites was not consistent, nor was it consistent with the weekday data. For PM_{10}, weekday and weekend results measured at Bloomsbury—Russell Square were comparable, as were the findings for CO at both background sites, at least in the direction of the changes if not in their magnitudes.

Effects of the CCS on Areas Outside the Zone

In the main analysis, temporal changes in pollutant concentrations measured at monitoring sites within the CCZ were compared with those in the control area. That approach left unused the data from a number of monitoring sites in the area surrounding the zone (between the boundary of the CCZ and 8 km from its center; see Figure 16). The descriptive analysis of data from all background sites (Figure 19) shows observed changes in geometric mean pollutant concentrations ordered by distance from the CCZ center. For NO, there was a clear decrease in the magnitude of changes before and after CCS implementation as the distance from the center of the CCZ increased. Changes related to distance from the zone center were also observed in the PM_{10} data but not so clearly as in the other pollutants investigated. It is possible therefore that the CCS may have had an impact on pollutant concentrations in the area surrounding the zone, although there may be other explanations for this observation.

Data Availability

A major restriction of this analysis was the lack of data from monitoring sites within the CCZ, particularly for roadside locations. Only a single monitor (Camden—Shaftesbury Avenue) provided roadside data for NO, NO_2, NO_x, and PM_{10}; no roadside site monitored CO over the 4-year period with sufficient capture rates for data analysis. Fortunately, for all but PM_{10}, data from background locations were available from more than one monitoring site within the CCZ. However, the analysis of the background CO data was restricted by the availability of only one comparison site in the control area. The lack of data from within the CCZ makes it difficult to distinguish between CCS effects and those specific to individual sites.

Potential Confounding

The statistical method used was chosen principally because it controlled for potential confounding effects of meteorologic and temporal patterns in pollutant concentrations across London as a whole. Hence, such factors should not confound the observed associations between the introduction of the scheme and the subsequent changes in pollutant concentrations. It is possible, however, that local factors could have unduly influenced temporal trends in the concentrations of a pollutant if missing data were concentrated in the period either before or after CCS implementation. The data availability criterion (75% of days with valid measurements) was applied to the whole 4-year period rather than separately to the periods before and after. An example of where this situation may have arisen is the analyses of the NO and NO_2 (but not NO_x) data at Bloomsbury—Russell Square and at Lewisham—Catford; those results gave rise to significant heterogeneity in the meta-analysis and contributed to the large decrease in relative pollution levels.

Choice of Time Period

The analysis period of 4 years, 2 before and 2 after the introduction of the CCS, was chosen to provide sufficient data to assess any potential impact of the scheme. By balancing the number of months on both sides of CCS implementation, the analysis was free from bias arising from imbalance in the months or seasons analyzed. Furthermore, the additional years of data also provided a broader temporal context for the analysis: The year the CCS was implemented was characterized by unusually hot temperatures and elevated pollutant concentrations (Fuller 2005). Although the atmospheric conditions that gave rise to this situation would have affected the control sites as well as the sites within the CCZ equally, the inclusion of additional years helped to lessen the sensitivity of the analyses to this rather unseasonal period of air pollution.

Serial Correlation in Pollutant Measurements

Daily concentrations of pollutants are serially correlated; the correlation arises from associations between temporal and meteorologic conditions and trends in pollutant sources over time. Such serial correlations between successive measurements can lead to problems in statistical models that assume independent errors. Violation of these assumptions leads to underestimating standard errors and finding inappropriately narrow confidence intervals. Given our emphasis on comparison of after/before ratios across different monitoring sites, contributions to autocorrelation that apply across London (e.g., weather) were not very relevant — they did not contribute to error in between-site comparisons in after/before ratios. A complete incorporation of likely correlated errors would thus ideally include not only temporally autocorrelated variation in data from each site, but also correlations between variations in daily concentrations in each pair of sites (e.g., due to weather or day of week). We decided this complexity was not warranted, because we used random-effects models, which can allow for any variation missed in estimated standard errors, to estimate the means of the after/before ratios across multiple comparison sites (i.e., the controlled ratios).

CONCLUSIONS

From the analyses presented and discussed above we draw the following conclusions:

- *Weekday Roadside*. Based upon the limited data available from within the CCZ, we found no evidence to suggest that the implementation of the CCS was associated with a change in roadside concentrations of NO_x, NO, and NO_2, within the CCZ relative to the control area during the hours the CCS was operated.
- *Weekday Background*. We also found little evidence to suggest that background concentrations of NO_x measured during the scheme's operation had changed relative to the control area after its implementation. This finding was based upon data from three monitoring stations within the CCZ and seven in the control area.
- *Weekday Background*. We found evidence to suggest that background concentrations of NO had decreased marginally within the CCZ compared with the control area after the CCS was implemented.
- *Weekday Background*. We found evidence to suggest that background concentrations of NO_2 had increased slightly within the CCZ compared with the control area after the CCS was implemented.
- *Weekday Background*. We found evidence to suggest that background concentrations of PM_{10} and CO fell within the CCZ compared with the control area, although these findings were based upon very limited data (a single site within the CCZ monitoring PM_{10} and a single site in the control area monitoring CO).
- *Weekend Background*. The analyses of changes in background concentrations of the five pollutants produced inconclusive results. The temporal changes in weekend pollutant concentrations within the CCZ compared with those in the control area were broadly comparable to those observed in the weekday analyses, although all weekend concentrations had fallen less than in the corresponding weekday comparisons. At face value these findings suggest that the changes observed at stations within the CCZ were not due to the implementation of the CCS alone but were also caused by other factors specific to those sites. However, there is some indication that the implementation of the CCS also altered traffic volumes and patterns on the weekends as well as on weekdays.
- *Weekday and Weekend Background*. Analyses of changes in pollution across London as a whole suggests, for some pollutants, that temporal changes in pollution differed according to the distance from the center of the CCZ.

SUMMARY OF INVESTIGATIVE ANALYSES

Four approaches were considered for use in the analysis of air pollution measurements in the CCS database. The previous section describes the approach by which the changes in mean pollutant concentrations from before to after the scheme was introduced were compared with changes at monitoring stations unlikely to be influenced by the CCS. This comparison of geometric means was agreed to be the most robust approach and was chosen as the analytical procedure to fully examine the CCS database.

Below is a summary of our experience with the three other analytical techniques that were applied to the CCS database and subsequently judged as requiring further development outside of the scope of this project. Despite their investigative nature, each technique provided useful supporting information for the main analyses. Each method and the results of its application are described in Appendices C (CUSUM statistical method), L (ethane dispersion) and M (bivariate polar plots), which are available on the HEI Web site.

USE OF ETHANE AS A DISPERSION INDICATOR

Background and Methods

Many influences work in concert to drive the hour-by-hour and day-by-day variability in air pollutant concentrations in London. To assess these other influences, we developed an analytical approach for a simple, observation-based analysis using the hydrocarbon ethane, which is typically attributed to natural gas leakage.

The short-term changes in local and London-wide pollutant concentrations (NO_2 and PM_{10}) were analyzed using ratified measurement data from 2 weeks before and 2 weeks after introduction of the scheme. Two sites were included in the PM_{10} analysis: Camden—Shaftesbury Avenue (Within Zone–Roadside) and Westminster—Marylebone Road (IRR–CCZ Boundary). The NO_2 analysis included two additional sites that did not monitor PM_{10}: Westminster—Horseferry Road and City of London—Senator House (both Within CCZ–Urban Background). The observed patterns in ethane concentrations were used to remove the influence of atmospheric dispersion and meteorology on individual pollutant concentrations.

Findings

Based on this approach, we concluded that when the changing influences of meteorology and atmospheric dispersion were taken into account, daily mean roadside PM_{10} concentrations may have decreased by 11% on the boundary of the CCZ and 24% within it. Roadside and background NO_2 concentrations on the CCZ boundary and within it may have decreased by between 29% and 33%. However, owing to the large day-to-day variability in daily mean PM_{10} and NO_2 concentrations, these before and after differences are unlikely to be statistically significant.

Strengths and Weaknesses

The use of ethane as a dispersion indicator removed the inherent variability in PM_{10} and NO_2 concentrations in London caused by changes in meteorology and atmospheric dispersion. In this way the technique had the potential to help identify more accurately the likely impacts of the CCS on London's air quality.

Although this novel method appeared promising over short time periods, a number of concerns were raised as to whether the leakage rate of ethane would remain constant and therefore provide a stable indicator of dispersion rates over longer time periods. Therefore we concluded that this method would need to be investigated further, which was outside the scope of this project. A full description of the work is provided in Appendix L (available on the HEI Web site).

APPLICATION OF THE CUSUM TECHNIQUE TO AIR POLLUTION DATA

Background and Methods

We hypothesized that the CUSUM statistical technique, developed for use in quality-control processes, might provide a simple method of identifying sustained step changes in pollution concentrations that might be related to the introduction of the CCS. The technique uses a simple equation to illustrate cumulative deviations from a reference value, in this case the mean concentrations in the 2 years before the CCS was implemented. It can be used to assess whether changes occur gradually over time or on a specific date.

Initial Findings and Subsequent Action

The technique was first tested by analyzing CO concentrations at a curbside monitoring site after the introduction of a bus lane adjacent to the site. The test case revealed that confounding influences on concentrations, most notably underlying trends and seasonality, complicated interpretation of the results from the CUSUM technique and the confounding influences acted to obscure change points in concentrations that the technique was intended to reveal. The CUSUM procedure was unable to differentiate between a change resulting from the CCS or from confounding influences; this led to the conclusion that the technique was only applicable to scenarios in which the expected change in concentration from the CCS was large in comparison with the change expected from confounding factors.

The CCS database was screened to identify those sites within the CCZ or in the area surrounding it that measured exceptional changes in geometric mean concentrations during CCH in the 2 years after CCS introduction compared with the 2 years before. The analysis was repeated for CO, NO_x, NO, NO_2, and PM_{10}. An exceptional change was defined as being more than 2 standard deviations from the mean change estimated from all monitoring sites in the CCS database. We applied CUSUM analysis to the sites to investigate whether the exceptional change occurred gradually or on an identifiable date.

Ultimate Findings

The CUSUM analysis did reveal step-changes in certain pollutants at one site within the CCZ and one site on its boundary that were sufficiently strong to overcome the confounders: a stepped increase in NO_2 levels at Westminster—Marylebone Road (CCZ boundary) and a stepped decrease in PM_{10} concentrations at Bloomsbury—Russell Square. The increase in NO_2 at Westminster—Marylebone Road could be dated within a few months after the introduction of the CCS (Figure 20). The decrease in PM_{10} was related to unusually high concentrations — attributed to construction work near the monitoring site — just before the CCS was introduced. We also found a decrease in NO_x concentrations at Tower Hamlets—Mile End Road (Inner London–Roadside), but our analysis was inconclusive.

Strengths and Weaknesses

The major strength of the CUSUM method over other methods used in this study is that it can potentially identify the approximate timing of changes that are thought to be associated with an intervention. However, its power to detect such a change is weakened by the effects of serial correlation within air pollution data caused by seasonality and long-term trends. The secure interpretation of CUSUM would require adaptation of the technique to take proper account of the underlying correlation between measurements, without the use of smoothing functions that would obscure a stepped change in concentrations.

Although the CUSUM screening study was not able to provide a quantitative estimation of changes in pollutant levels that may have arisen from the introduction of the CCS, those strong signals that were identified should be considered in the context of other results in the CCS study. A full description of this approach is provided in Appendix C (available on the HEI Web site).

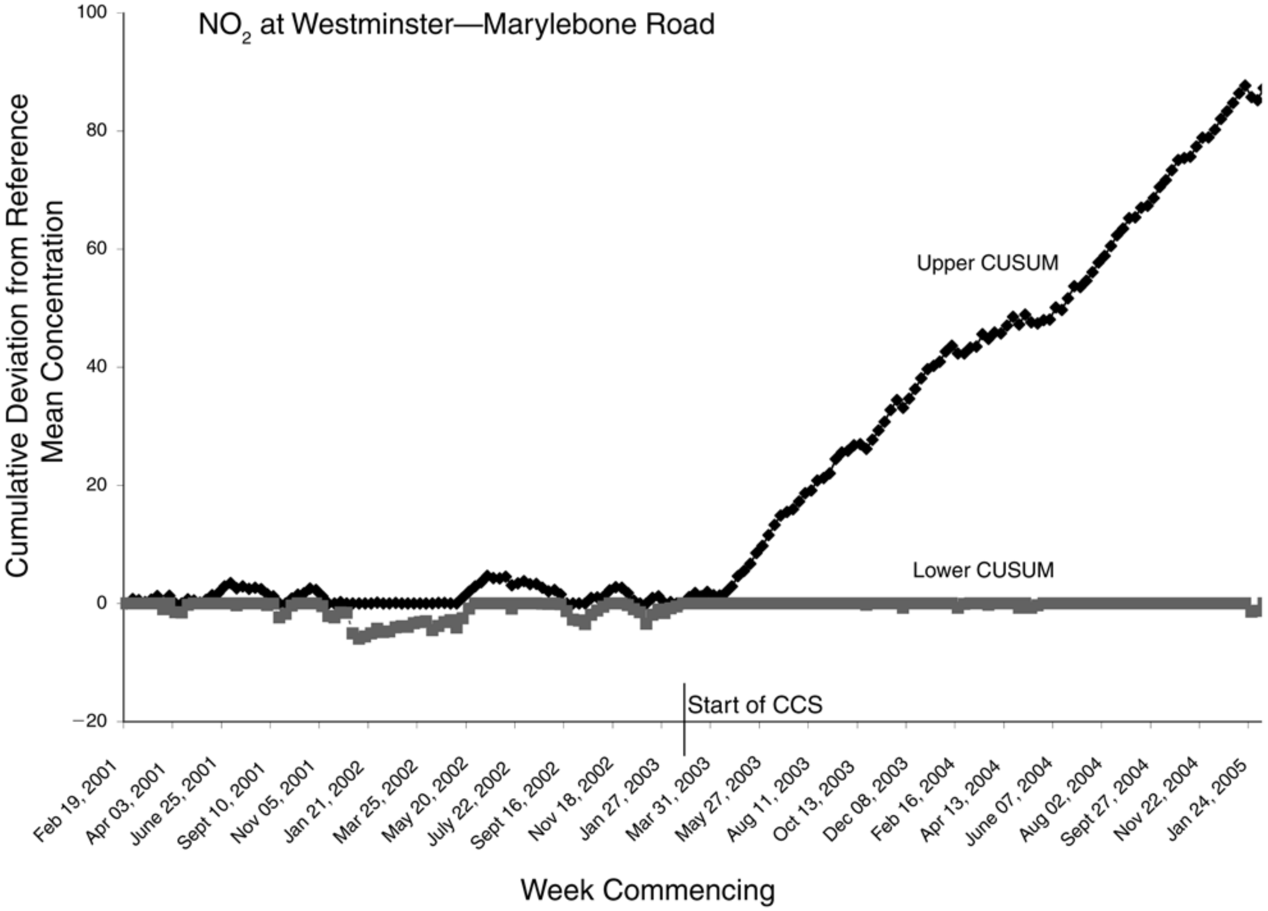


Figure 20. CUSUM chart of NO_2 at Westminster—Marylebone Road curbside site, on the CCZ boundary, showing a signal in the upper CUSUM sufficiently strong to overcome the effects of seasonality. Data are for CCH only. Start of CCS on February 17, 2003, is noted.

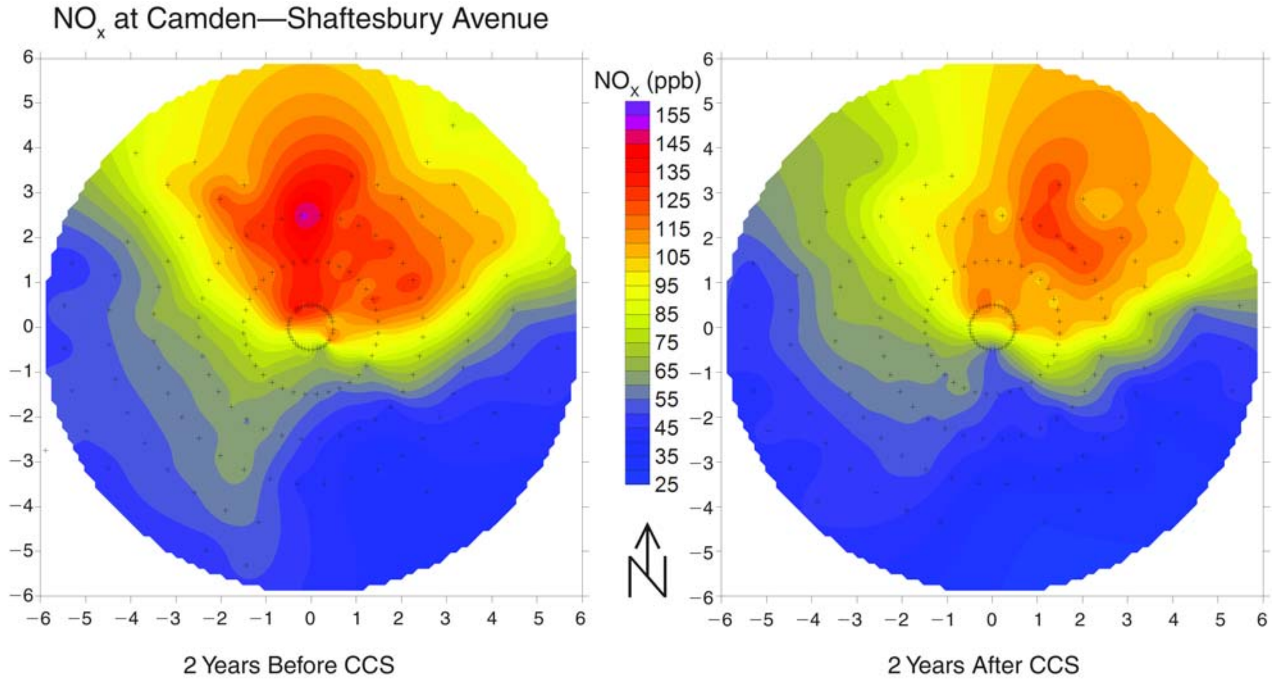


Figure 21. Polar plots for NO$_x$ at Camden—Shaftesbury Avenue within the CCZ. Crosses show input grid data points. Wind speed is represented on the radial axis (center outward; 0 to 6 m/sec), wind direction is shown on the polar axis (around the circumference).

USE OF BIVARIATE POLAR PLOTS TO CHARACTERIZE LOCAL EMISSIONS

Introduction and Methods

The bivariate polar plot analysis was designed to identify the portion of the NO_2, NO_x, and PM_{10} data from the single roadside site within the CCZ (Camden—Shaftesbury Avenue) that could be directly related to emissions from the road immediately adjacent to the monitoring site. Bivariate polar plots provide a graphical representation of the wind speed and directional dependence of any measurement at a particular monitoring site. This is a qualitative method of identifying the location and certain characteristics of primary emission sources surrounding a monitoring site and their likely contribution to overall mean concentrations at the site.

This analysis used 15-minute mean pollutant measurements taken during the CCH at the Camden—Shaftesbury Avenue site combined with wind speed and direction data to produce an input grid. This grid was then processed by a surface mapping program, using kriging to interpolate between grid points, to produce the polar plots. Regional pollution sources were removed by subtracting corresponding mean concentrations from the composite mean of the Suburban Outer London indicator sites (as defined in Table 13). The difference between the local measured concentration and the Suburban Outer London composite concentration represented the concentration arising from local sources. The polar plots were then used to identify the roadside emission portion (i.e., an estimate of mean concentrations arising specifically from emissions on the road immediately adjacent to the site).

By comparing mean concentrations of NO_x, NO_2, and PM_{10} identified as the roadside emission portions in the 2 years before and after introduction of the CCS, an assessment could be made as to whether the intervention had affected emissions at the roadside CCZ site, while minimizing the effects of larger-scale changes in ambient pollutant concentrations due to meteorologic variation.

Findings

Figure 21 shows polar plots for NO_x at Camden—Shaftesbury Avenue with separate plots for the two years before and after the CCS was introduced. The radial axis of each plot shows wind speed from 0 m/sec in the center to 6 m/sec on the perimeter. The polar axis [around the circumference] represents wind direction. The contours show the smoothed mean NO_x concentration in ppb. The highest NO_x concentrations were recorded during northerly or northeasterly winds between 0 and 4 m/sec.

The use of bivariate polar plots in this application revealed important characteristics of the monitoring data set from the only roadside site within the CCZ. First, this analysis highlighted the importance of considering prevailing weather conditions when positioning a roadside monitor. The Camden—Shaftesbury Avenue site is located on the southwest side of a busy junction. The wind frequency analysis showed that although the main pollutant source was to the northeast, winds from that direction were very infrequent (18% before CCS, 15% after CCS of the total for wind directions between 330° and 80°, wind speeds 1 to 4 m/sec). If this monitoring site were located on the opposite side of the junction, mean concentrations of NO_x, NO_2, and PM_{10} would have been higher, and detecting a traffic-related change in pollutant concentrations related to the CCS implementation may have been more likely.

The contour plots also provided a visual indication of the meteorologic conditions that gave rise to peak concentrations of each pollutant and highlighted the road junction to the northeast of the monitoring site as being the principal source of NO_x and NO_2 and, to a lesser degree, PM_{10}. A comparison of plots in the period 2 years before and after the intervention gave an indication of changes in mean concentrations relating to vehicle emissions from this principal source (Figure 21, Table 26).

This analysis shows that the decrease in NO_x concentrations measured during charging hours at Camden—Shaftesbury Avenue over the 4-year period was driven by decreases in emissions primarily from the road to the north-east of the monitoring site. However, the method was unable to differentiate between the effects of improved vehicle emissions technology (independent of the CCS) and the effects of decreased vehicle numbers as a result of the CCS.

The NO_2 analysis revealed little or no change in NO_2 measurements that could be attributed to emissions from the principal road source to the northeast.

A high incidence of calm conditions and easterly winds, which increase transboundary transport of particulate pollution, led to unusually high PM_{10} concentrations across London after introduction of the CCS in 2003. Although the bivariate polar plot method accounts for regional sources of PM_{10} pollution, decreased dispersion rates associated with these easterly winds caused unusually high concentrations of PM_{10} arising from sources within London itself. The PM_{10} polar plot analysis reflected this in increased concentrations from a range of wind conditions (see Appendix M).

However, the disproportionately large increase in peak concentrations from the primary emissions source to the northeast of the monitoring site suggests that local PM_{10} emissions may also have increased. The reasons for the PM_{10} increase are not obvious, but may be related to a change in vehicle mix from gasoline-to diesel-powered vehicles due to the large increase in taxi use.

Strengths and Weaknesses

The novel use of bivariate polar plots in this application proved useful by revealing important characteristics of the monitoring dataset from the only roadside site within the CCZ and by highlighting the importance of considering prevailing weather conditions when positioning a roadside monitor.

The analysis would benefit from further development, notably in transforming the qualitative assessment of change into a quantitative assessment and including an estimation of the uncertainty of outputs. Research is ongoing to develop this method in a range of air quality time-series studies. A full account of that work is provided in Appendix M (available on the HEI Web site).

INTEGRATED DISCUSSION

In February 2003, a CCS was introduced in London with the aim of reducing traffic within the congested central area of the city. The CCS has proved to be successful at meeting this objective. After 1 year of operation (2003), traffic (vehicles with four or more wheels) entering the charging zone during charging hours had decreased by

Table 26. Statistical Summary of Interpolated Output Grid Concentrations from Camden—Shaftesbury Avenue[a]

Input Data	Minimum	Mean	Maximum	SD	Upper Quartile Mean	Upper Quartile Change
NO_2 pre-CCS (ppb)	16.2	26.2	44.6	6.0	34.9	3%
NO_2 post-CCS (ppb)	16.5	26.2	41.3	6.6	36.0	
NO_x pre-CCS (ppb)	34.6	76.0	151.8	30.1	117.8	−7%
NO_x post-CCS (ppb)	27.8	69.7	127.5	28.5	109.9	
PM_{10} pre-CCS (µg/m^3)	3.5	11.3	19.8	3.0	15.1	6%
PM_{10} post-CCS (µg/m^3)	4.0	11.9	20.3	3.3	16.0	

[a] CCH only. Outer London composite control concentrations were subtracted.

18% and these reductions have been maintained. Traffic entering the CCZ during 2006 was 21% lower than in 2002 (TfL 2007). The question addressed in this study is, Did the reduced number of vehicles translate into an improvement in air quality in London?

To examine this question we used a number of methods to estimate, predict, and measure possible air quality changes within the CCZ and outside it in the first two years of the scheme's operation. We used emissions and air pollution modeling techniques and data derived from the extensive air quality monitoring network available in London. Several methods were being developed for this study and considerable effort was invested in improving approaches to investigate the impact of traffic management schemes. The approaches and results from this project, therefore, have the potential to inform future decisions about road pricing schemes that are being considered in other cities around the world and to provide a framework for analyzing results from such studies.

MODELING STUDIES OF THE LIKELY AIR QUALITY IMPACTS OF THE CCS

Our modeling work compared periods before (2001 and 2002) and after (2003 and 2004) CCS implementation, and concentrations of NO_x, NO_2, and PM_{10} were expressed as annual mean values. By comparing mean values within the CCZ with those in the remainder of Greater London, a possible CCS impact was calculated.

The results projected that NO_x concentrations would decrease between the pre- and post-CCS periods. The average difference in NO_x concentrations was projected to be −3.6 ppb within the CCZ and −1.9 ppb for the area outside (Table 4). If the impact of the CCS were removed, the projected change in NO_x in the CCZ would be approximately the same as the value for Greater London; we concluded that introducing the CCS would decrease NO_x levels by an average of 1.7 ppb within the CCZ.

The expected change in NO_2 concentrations showed a similar spatial distribution as that for NO_x, although the absolute changes were projected to be very small. Predicting NO_2 levels was complicated by a small increase in primary NO_2 both before and after the CCS began, which varied road by road. Comparing the average concentrations within and outside the zone, we predicted that introducing the CCS would increase NO_2 concentrations by 0.3 ppb within the CCZ.

Modeled PM_{10} concentrations were projected to decrease slightly from before to after CCS implementation: Comparing the average PM_{10} concentrations within and outside the zone, we predicted that introducing the CCS would be associated with net decrease in the mean PM_{10} concentrations of 0.8 $\mu g/m^3$ within the CCZ (Table 4).

Our modeling investigations had two potential limitations. First, the changes in individual pollutant levels predicted in this simple comparison were dominated by data from background locations and are likely to be smaller than possible impacts at roadsides, where the influence of the CCS is likely to be strongest. Second, the analysis assumed that any emission trends that were not associated with the CCS would have similar effects within and outside the zone and that the model would perform equally well in both areas.

To evaluate these limitations we conducted model sensitivity tests in which we broke down different sources of NO_x and PM_{10} emissions within and outside the zone. The modeling transect plots of data for NO_x (Figure 12) and PM_{10} (Figure 13) show that the contribution of pollutants from road traffic is likely to be very dependent on the monitoring site's location; therefore, modeled changes expected to be brought about by the CCS would not only vary depending on the road but also on the relative contribution of local sources. The consequence of this is that the analysis of data from a single roadside site (as was available within the CCZ) cannot be assumed to reflect the overall changes of the CCS. To overcome this limitation in our analysis, we added data from a range of background sites across Greater London where sources can be attributed more consistently, but which have less traffic.

An additional complication identified by the modeling studies is that any small change in pollutant concentrations brought about by the CCS may compete with pollutant contributions from outside the zone that may be of similar or greater magnitude and thus hide the impact of the CCS. For example, the model transect plots showed that, compared with NO_x, a much larger component of PM_{10} could be attributed to emission sources outside of London than to local traffic. Hence, changes brought about by the CCS might be overshadowed by larger regional concentrations and thus, in measurement data, may result in only a small absolute change in PM_{10} concentrations.

A recommendation for future studies of this kind would be to determine ahead of time the London increment of PM_{10} (London PM_{10} − rural PM_{10}), or where there are more roadside sites, determine the roadside increment of PM_{10} (roadside PM_{10} − nearby background PM_{10}). This approach would provide a broader range of differences in concentrations across the CCZ and possibly allow for a more distinguishable signal of effects associated with any traffic changes.

STATISTICAL ANALYSIS OF MEASUREMENT DATA

For the analysis of measured pollutants, we established a CCS database from ratified measurements obtained from the LAQN. Once this was done, four approaches were considered for analyzing the data. Three approaches were all found to be of use but each had limitations that could not be resolved within the time frame of the project. Of the four, comparison of geometric means was agreed to be the most robust approach and a full examination of the CCS database was carried out with this analytical procedure.

Geometric means from 2 years before and 2 years after the introduction of the scheme were compared. Temporal changes at roadside and background monitors within the CCZ were compared with changes over the same periods at similarly sited monitors in the control area more than 8 km from the CCZ center. The analysis focused on the hours (and days) on which the scheme was in operation and on vehicle-derived pollutants (NO, NO_2, NO_x, PM_{10}, and CO). Based upon the limited data available from within the CCZ we found:

- Roadside: no evidence to suggest changes in NO_x, NO, and NO_2 concentrations;
- Background: little evidence to suggest changes in NO_x concentrations;
- Background: evidence to indicate NO concentrations decreased and NO_2 concentrations increased; and
- Background: some evidence to suggest that PM_{10} and CO concentrations decreased.

A further analysis of the changes in pollutants across London suggested that the temporal changes for some pollutants differed according to a site's distance from the center of CCZ.

In establishing the analytical framework for this work, a number of key decisions were considered and agreed upon by the investigative team. Each of these is described below to illustrate the challenges and limitations associated with our analyses.

Data Availability

A major restriction of the geometric mean analysis was that only a single roadside monitor within the CCZ (Camden—Shaftesbury Avenue) was in operation. This made it difficult to distinguish between CCS effects and those specific to individual sites. Fortunately, for all but PM_{10}, data from background locations were available from more than one monitoring site within the CCZ. Therefore, it was possible to assess the temporal changes in pollution more generally within the CCZ and increase our confidence in the changes we identified.

Background Versus Roadside

Our initial hypothesis was based on the belief that any effects of the CCS would most readily be observed in data collected at monitoring stations located at the roadside. Because of the limited number of roadside sites, we included data from background monitoring stations in the analysis. (This choice was also justified by the widespread use of background monitors in epidemiologic studies of the health effects of outdoor air pollution.) We found little evidence for CCS-related changes in data from the one roadside monitor located within the CCZ, whereas the evidence for temporal changes at background locations was more compelling (for some pollutants). As our work with the bivariate polar plot technique revealed (Appendix M), it is possible that roadside locations are highly site-specific and affected by local conditions far more than stations situated in background locations.

Potential Confounding

Air pollution in London arises from local and regional sources, and temporal trends are influenced by a number of factors including the age and performance of vehicles, changes in traffic volume, and meteorologic conditions. Therefore, to evaluate temporal trends in a small area in the center of London, it was essential that all analyses be adjusted for trends in air pollution concentrations across London as a whole. The statistical method employed was therefore designed to achieve this control; hence, such factors should not confound the observed associations between the introduction of the scheme and the subsequent changes in pollutant concentrations. This adjustment is central to the analysis of measurement data and to one's belief in the validity and reliability of the estimated changes in pollution within the CCZ. The finding that the temporal changes in pollution at background stations within the CCZ were homogeneous with those at similar stations in the control area is therefore an important one. It suggests that — for background pollutant concentrations at least — there is a consistent regional trend against which to evaluate the changes within the CCZ.

Choice of Time Period

The analysis period 2 years before and 2 years after the CCS was introduced was chosen to provide sufficient data to assess any potential CCS impact. By balancing the number of months on either side of the implementation, the analysis was free from bias owing to imbalance in the months or seasons analyzed. Unexpectedly, the year the CCS was implemented (2003) was characterized by unusually hot temperatures and elevated pollutant concentrations (Fuller 2005). Although the atmospheric conditions that gave rise to this unusual situation would have affected the control sites and sites within the CCZ equally, the inclusion of additional years helped to lessen the sensitivity of the analyses to this rather unseasonal period of air pollution.

The possibility still remains that local factors could have unduly influenced temporal trends in the concentrations of a pollutant when, for any analysis, the proportion of missing data was concentrated either before or after CCS implementation (as evidenced by data from Lewisham—Catford). The data availability criterion for monitoring sites (75% of days with valid measurements) was applied to the whole 4-year time period to minimize the impact of missing data on the analysis. However, it may have been more appropriate to apply this criterion separately to the before and after periods. Given the isolated examples highlighted above however, this possible limitation of the analysis is not considered to be major.

Serial Correlation in Pollutant Measurements

Daily concentrations of pollutants are known to be serially correlated; the correlation arises from temporal associations with meteorologic conditions and from trends in pollutant sources over time. Such serial correlations among successive measurements can lead to problems in statistical models that assume independent errors. Given our emphasis on after/before ratios across different monitoring sites, sources of autocorrelation that apply across London (e.g., weather) are not very relevant — they do not contribute to error in between-site comparisons in after/before ratios. A complete incorporation of likely correlated errors would thus include not only temporally autocorrelated variation in data from each site, but also correlations among variations in daily concentrations in each of a pair of sites (e.g., due to weather or day of the week). We decided that this complexity was unwarranted, because to estimate the means of the after/before ratios across multiple comparison sites we used random-effects models, which can allow for any variation missed in estimated standard errors.

Weekend Analysis

The purpose of weekend analyses was to provide a further control for the weekday analyses. That is, by investigating data that should be free from any effects of the CCS and yet are subject to the same temporal and seasonal confounders present in the main analyses, we expected to provide evidence that would either support or undermine the conclusion that the implementation of the CCS would affect some air pollutant concentrations. If the CCS were indeed responsible for the greater-than-expected relative fall in background NO and PM_{10} concentrations during the hours of CCS operation on weekdays, then one would not expect to see the same change in pollutants during weekends when the CCS was not in operation. This assumption was based upon the premise that the effects of the CCS were limited to its hours of operation. The picture that emerged from this analysis was initially unexpected; broadly speaking, the temporal changes in pollution observed on weekends were much the same as those observed during weekdays. Data were subsequently obtained from TfL that suggested the CCS also influenced traffic volumes on weekends, which provides a possible explanation for these findings.

Effect of the CCS on Areas in Greater London Outside the Zone

The main analysis was extended to include monitoring sites in the area surrounding the zone (between the boundary of the CCZ and 8 km from its center). This analysis suggested that, for background concentrations of NO, there was a decrease in the magnitude of changes before and after CCS implementation as the distance from the center of the CCZ increased — a result also observed to some extent in the weekend data. Changes related to distance from the CCZ center were also observed in the PM_{10} and the CO data, but not so clearly as in the other pollutants investigated. It is possible, therefore, that the CCS may have had an impact on pollutant concentrations in the area surrounding the CCZ, although there may be other explanations.

SYNTHESIS OF FINDINGS

Our investigation has confirmed that assessing the impact of traffic management schemes on urban air quality is complex and challenging. In this project, our analyses were limited by needing to rely on air pollutant measurements from existing monitoring sites that did not precisely fit the objectives of the study. For example, only a few monitoring sites were situated within the CCZ, and only one of those was at a roadside. In contrast, extensive measurements were available for comparison at sites outside the zone across Greater London.

On interpreting results from all of our analyses — air pollutant emissions and dispersion modeling, comparing geometric means, and exploring alternative analytical approaches including the use of ethane as a dispersion indicator, the CUSUM method to detect temporal step changes in pollutant concentrations, and bivariate polar plots to characterize source influences on monitoring sites — we found that small changes in air quality in the CCZ were associated with the introduction of the scheme. These included small decreases in background PM_{10} and larger decreases in background NO and possibly in background CO. Small increases were noted in background levels of NO_2.

It is likely that other air pollution control measures introduced along with the CCS influenced air quality. We drew this conclusion in part from the spatiotemporal changes in air quality we observed during the weekends when the CCS was not in operation. The rise in NO_2 is plausibly explained by the bus fleet having been fitted with regeneration particle traps, as well as a general increase in diesel-fueled vehicles. The fall in background NO within the CCZ might be associated with an increase in ozone, and this is currently being investigated.

IMPLICATIONS FOR OTHERS INTRODUCING TRAFFIC MANAGEMENT SCHEMES TO IMPROVE AIR QUALITY

In summary, this project utilized a range of modeling and measurement techniques to investigate whether the reduction in congestion and traffic, achieved in London after the introduction of the CCS in February 2003, has brought about associated changes in air quality within the first few years of operation. Each technique had its own advantages and limitations, which, in combination, provided separate estimates of outcomes. The emissions modeling exercise projected a high-resolution London-wide estimate of change on a scale that would not be possible if we used actual measurements from the limited number of monitoring sites. The evaluation of air monitoring data compared the geometric mean concentrations of individual pollutants from a large number of monitoring sites to identify differences between London-wide trends independent of the CCS and trends within the CCZ. This method produced a quantitative estimate of the effects of the CCS at roadside and background sites within the CCZ. The ethane dispersion adjustment model used a novel method of accounting for dispersion parameters, but was limited to the period immediately after introduction of the scheme. Although the CUSUM approach was weakened by seasonality and underlying trends, it was able to give some indication of the timing of strong changes in pollutant concentrations at certain sites. The bivariate polar plot technique was effective in isolating the specific local component of emissions, but its use was limited to the single roadside site within the CCZ and was largely qualitative.

Collectively, the various analyses conducted in this study support the following conclusions about the influence of the CCS and offer important insights for future investigations into the impact of major traffic management schemes on air pollutant emissions and air quality.

1. The CCS, introduced in February 2003, was applied to a small central area of Greater London. An important and recurring finding of this study was that the area was too small to influence air pollution concentrations to any great extent, either within the CCZ or outside it. In February 2007 the zone was extended westward to double its size. This increased area is likely to increase the influence of the CCS on pollutant concentrations.
2. Small signals of air quality changes were observed; if they are accurate, they suggest that such a traffic management scheme could provide an air quality benefit. However, the study results also highlight the potential for detrimental effects. Despite a marked decrease in vehicle numbers, a shift in the vehicle fleet profile from gasoline- to diesel-powered vehicles and the addition of emissions control technology for buses may have led to an increase in NO_2 concentrations at some locations within and outside the zone.
3. The modeling analysis showed that a large proportion of PM_{10} is expected to be associated with wider-scale regional contributions and as a consequence, the impact of traffic management on PM_{10} concentrations is likely to result in only modest changes measured at background monitors. This would not necessarily be the case close to roads, where a larger impact of traffic management would be expected.
4. Modeled emission estimates indicated that PM_{10} from tire and brake wear is an increasingly important component of vehicle emissions; and given that exhaust emissions are predicted to fall in future years, non-exhaust vehicle emissions are likely to increase in importance. This has important consequences for traffic management schemes that promote a reduction in congestion only; such reductions may have an additional effect on this source of PM.
5. Monitoring sites need to be carefully placed to reliably assess any impact of a traffic management scheme; reliance on a small number of sites limits what can be concluded. A monitoring program should be in place well before a scheme's intervention date and should be designed to include locations expected to show the greatest change in pollutant levels as well as those that are representative of background levels. Monitoring a wide range of pollutant species, and including particle speciation that might enable source attribution, should be considered. Finally, accurate vehicle profiling and local meteorologic parameters adjacent to the roadside monitoring sites should be included. This would allow a more direct relationship to be established between vehicle emissions and ambient monitoring data than

was possible in this study. (Such a monitoring program was established across London in 2006 tailored specifically to provide monitoring data for a subsequent assessment of changes in pollution levels in response to the London Low Emission Zone [Kelly et al. 2011], which was implemented in February 2008.)

6. A major strength of the current study is the use of diverse assessment techniques — emissions modeling, statistical analysis of monitoring data, and alternative laboratory-based metrics for characterizing the potential toxicity of ambient PM (reported in *Part 2. Analysis of the Oxidative Potential of Particulate Matter*). The combination of results provides a fuller, more holistic picture of the influence of the CCS than would have been possible using a single analysis strategy. The power of such a combined assessment strategy could be strengthened further by closer integration. For example, outputs from the laboratory-based analyses of PM could be fed back into a dispersion model to produce a map of particulate toxicity across London; and collecting traffic count data at measurement sites could help understand the role of traffic characteristics in the interpretation of results.

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APPENDIX A. HEI Quality Assurance Statement

The conduct of this study was subjected to independent audits by Dr. Richard Kwok and Dr. James Flanagan of RTI International. Kwok and Flanagan are experts in quality assurance for air quality monitor studies and related epidemiologic studies. The audits included on-site reviews of study activities for conformance to the study protocol and standard operating procedures. The dates of the audits and the phases of the study examined are given below.

December 6–8, 2006 (Phase 1)

The auditors conducted an on-site audit at King's College London to verify the integrity of the reported data. The audit reviewed the following study components: progress reports, personnel and staff, adequacy of equipment and facilities, internal quality assurance procedures, air quality sampling methods, and data processing procedures. Several data points for each parameter were traced through the entire data processing sequence to verify that the described procedures had been followed and to verify the integrity of the database. The audit also included spot checks of the monitoring stations' original data records against the project database for any data transcription errors. No errors were noted.

April 3–4, 2008 (Phase 2)

The auditor conducted on-site audits at St. George's Hospital in London and King's College London. The auditors assessed the investigators' responses to the phase 1 audit and extended the review to the health data being compiled by investigators at St. George's Hospital.

July–August, 2009 (Phase 3)

The auditors reviewed the Draft Final Report to ensure data issues noted earlier were addressed. No further issues were noted.

Written reports of the Quality Assurance oversight inspections were provided to the HEI project manager, who transmitted the findings to the Principal Investigator. These quality assurance oversight audits demonstrated that the study was conducted by a well-coordinated, experienced team according to the study protocol and standard operating procedures. Interviews with study personnel revealed a consistently high concern for data quality. The report appears to be an accurate representation of the study.

Richard Kwok

Richard K. Kwok, Ph.D.
Epidemiologist, Quality Assurance Officer

James B Flanagan

James Flanagan, Ph.D.
Chemist, Quality Assurance Officer

APPENDIX B. Background and Roadside Monitoring Sites in Greater London Used in the Temporal Analyses of Changes in Mean Measured Pollutant Concentrations

Table B.1. Background Monitoring Sites in Greater London Used in the Time-Series Analysis[a]

Monitoring Site	Pollutants Monitored	Distance from Center of CCZ (km)	Data Collection Period
Within CCZ			
Bloomsbury—Russell Square	NO_x, PM_{10}, CO	1.5	2/17/2001–2/16/2005
City of London—Senator House	NO_x	1.5	10/10/2001–2/16/2005
Westminster—Horseferry Road	NO_x, CO	1.9	7/17/2001–2/16/2005
Inner London			
Southwark—Elephant and Castle	NO_x, PM_{10}, CO	2.5	2/17/2001–2/16/2005
Islington—Upper Street	NO_x, PM_{10}	3.6	2/17/2001–2/16/2005
Tower Hamlets—Bethnal Green	NO_x, PM_{10}	4.8	2/17/2001–2/16/2005
Lambeth—Loughborough Junction	NO_x, PM_{10}	5.1	12/19/2001–2/16/2005
K & C—West London	NO_x, CO	6	2/17/2001–2/16/2005
Tower Hamlets—Poplar	NO_x, PM_{10}	6.7	2/17/2001–2/16/2005
K & C—North Kensington	NO_x, PM_{10}, CO	6.9	2/17/2001–2/16/2005
Hackney—Clapton	NO_x, CO	7	2/17/2001–2/16/2005
H & F—Brook Green	*NO_x, PM_{10}*	*7.3*	*7/28/2003–2/16/2005*
Wandsworth—Town Hall	NO_x, CO	7.8	2/17/2001–2/16/2005
Outer London			
Greenwich—Millennium Village	*NO_x, PM_{10}*	*9.5*	*8/1/2004–2/16/2005*
Waltham Forest—Dawlish Road	NO_x, PM_{10}	9.7	2/17/2001–2/16/2005
Lewisham—Catford	NO_x	9.8	2/17/2001–2/16/2005
Barnet—Strawberry Vale	*NO_x, PM_{10}*	*10.9*	*2/17/2001–5/15/2002*
Barnet—Finchley	NO_x, PM_{10}	11.1	2/17/2001–2/16/2005
Ealing—Ealing Town Hall	NO_x	13.4	2/17/2001–2/16/2005
Enfield—Salisbury School Ponders End	NO_x, PM_{10}, CO	15.1	2/17/2001–2/16/2005
Redbridge—Perth Terrace	NO_x, PM_{10}	15.3	2/17/2001–2/16/2005
Sutton—North Cheam	*NO_x*	*16.4*	*2/17/2001–5/3/2002*
Harrow—Stanmore Background	NO_x, PM_{10}	17.3	2/17/2001–2/16/2005
Ealing—Southall	*NO_x, PM_{10}*	*19.1*	*7/13/2004–2/16/2005*
Hillingdon—Harlington	*NO_x, PM_{10}*	*22.7*	*1/1/2004–2/16/2005*
Heathrow Airport	NO_x, PM_{10}, CO	22.7	2/17/2001–2/16/2005

[a] Sites *shown in italic type* were excluded at the first stage of analysis due to data-capture rates < 75% over the 4-year collection period.

Table B.2. Roadside Monitoring Sites in Greater London Used in the Time-Series Analysis[a]

Monitoring Site	Pollutants Monitored	Distance from Center of CCZ (km)	Data Collection Period
Within Charging Zone			
Camden—Shaftesbury Avenue	NO_x, PM_{10}	1	2/17/2001–2/16/2005
Inner London			
K & C—Knightsbridge	NO_x	3.5	2/17/2001–2/16/2005
K & C—King’s Road	NO_x	4.3	2/17/2001–2/16/2005
K & C—Cromwell Road	NO_x, PM_{10}, CO	4.6	2/17/2001–2/16/2005
Southwark—Old Kent Road	NO_x, PM_{10}, CO	4.8	2/17/2001–2/16/2005
Islington—Holloway Road	NO_x, PM_{10}, CO	5.2	2/17/2001–2/16/2005
Tower Hamlets—Mile End Road	NO_x, CO	5.4	2/17/2001–2/16/2005
Camden—Swiss Cottage	NO_x, PM_{10}	5.7	2/17/2001–2/16/2005
Lewisham—New Cross	NO_x, PM_{10}	6.6	3/31/2002–2/16/2005
Lambeth—Christchurch Road	NO_x, PM_{10}	7.3	2/17/2001–2/16/2005
H & F—Hammersmith Broadway	NO_x, PM_{10}	7.6	2/17/2001–2/16/2005
Wandsworth—High Street	NO_x, PM_{10}, CO	7.9	2/17/2001–2/16/2005
Outer London			
Greenwich—Blackheath	NO_x, PM_{10}	8.3	3/8/2002–2/16/2005
Greenwich—Trafalgar Road	NO_x, PM_{10}	8.6	2/17/2001–2/16/2005
Richmond—Castlenau	NO_x, PM_{10}	9	2/17/2001–2/16/2005
Brent—Harlesden	*NO_x, PM_{10}*	*9.7*	*10/31/2001–2/16/2005*
Greenwich—Woolwich Flyover	*NO_x, PM_{10}*	*9.7*	*7/8/2004–2/16/2005*
Crystal Palace—Crystal Palace Parade	NO_x, PM_{10}, CO	9.9	2/17/2001–2/16/2005
Hounslow—Chiswick High Road	NO_x, PM_{10}	10	2/17/2001–2/16/2005
Waltham Forest—Mobile	*NO_x, PM_{10}*	*10.4*	*2/17/2001–10/12/2001*
Ealing—Acton Town Hall	NO_x, PM_{10}, CO	10.5	2/17/2001–2/16/2005
Haringey—Town Hall	NO_x, PM_{10}	10.5	2/17/2001–2/16/2005

Table continues next page

[a] Sites *shown in italic type* were excluded at the first stage of analysis due to data-capture rates < 75% over the 4-year collection period.

Table B.2 (*Continued*). Roadside Monitoring Sites in Greater London Used in the Time-Series Analysis[a]

Monitoring Site	Pollutants Monitored	Distance from Center of CCZ (km)	Data Collection Period
Outer London (*Continued*)			
Haringey—Bounds Green	*NO_x, PM_{10}*	*10.8*	*2/17/2001–3/11/2001*
Brent—Ikea Car Park	*NO_x, PM_{10}*	*11.1*	*6/17/2001–2/16/2005*
Brent—Ikea	*NO_x, PM_{10}*	*11.1*	*6/20/2003–2/16/2005*
Enfield—Bowes Road	*PM_{10}*	*11.7*	*7/1/2004–2/16/2005*
Ealing—Hanger Lane	*NO_x*	*12.4*	*8/4/2003–2/16/2005*
Greenwich—Westhorne Avenue	*NO_x, PM_{10}*	*12.4*	*10/1/2004–2/16/2005*
Enfield—Derby Road Upper Edmonton	NO_x, PM_{10}	12.6	2/17/2001–2/16/2005
Redbridge—Gardner Close	NO_x, PM_{10}, CO	12.7	2/17/2001–2/16/2005
Redbridge—Southend Road	*NO_x, PM_{10}, CO*	*13.2*	*11/19/2003–2/16/2005*
Greenwich—Burrage Grove	*NO_x, PM_{10}*	*13.3*	*10/7/2004–2/16/2005*
Hounslow—Brentford	*NO_x, CO*	*13.5*	*2/17/2001–1/1/2003*
Hounslow—Brentford	*PM_{10}*	*13.5*	*2/17/2001–1/1/2003*
Hounslow—Brentford	*NO_x, PM_{10}, CO*	*13.6*	*6/2/2003–2/16/2005*
Waltham Forest—Chingford	*NO_x, PM_{10}*	*14.4*	*7/14/2003–2/16/2005*
Bromley—Central	NO_x, PM_{10}, CO	14.8	2/17/2001–2/16/2005
Croydon—George Street	NO_x, PM_{10}	15	2/17/2001–2/16/2005
Greenwich Bexley—Falconwood	NO_x, PM_{10}	15.2	2/17/2001–2/16/2005
Enfield—Church Street	NO_x, PM_{10}, CO	16.1	2/17/2001–2/16/2005
Croydon—Purley Way	NO_x	16.3	2/17/2001–2/16/2005
Sutton 1—Town Centre	*NO_x, PM_{10}, CO*	*17*	*2/17/2001–4/26/2002*
Wandsworth—A3	NO_x, PM_{10}, CO	19.1	2/17/2001–2/16/2005
Harrow—North Harrow Roadside	*NO_x, PM_{10}*	*19.2*	*2/17/2001–2/16/2005*
Hillingdon—South Ruislip	NO_x, PM_{10}	20.5	2/17/2001–2/16/2005
Havering—Romford	NO_x, PM_{10}	21.7	2/17/2001–2/16/2005
Bexley—Thames Road North	*NO_x, PM_{10}*	*22.4*	*4/8/2004–2/16/2005*
Bexley—Thames Road South	*NO_x, PM_{10}*	*22.4*	*4/6/2004–2/16/2005*
Havering—Rainham	NO_x	22.6	2/17/2001–2/16/2005
Hillingdon—Hillingdon Hospital	*NO_x, PM_{10}*	*23.8*	*9/25/2002–2/16/2005*

[a] Sites *shown in italic type* were excluded at the first stage of analysis due to data-capture rates < 75% over the 4-year collection period.

APPENDICES AVAILABLE ON THE WEB

Appendices C through M contain supplemental material not included in the printed report. They are available on the HEI Web site at *http://pubs.healtheffects.org*.

Appendix C. Investigation of the Cumulative Sum Technique to Analyze Air Quality Changes

Appendix D. London Atmospheric Emissions Inventory — Road Traffic Emissions Summary

Appendix E. Air Pollution Modeling Methods

Appendix F. Model Performance for the Years 2001 to 2004

Appendix G. Summary Statistics and Time-Series Charts of Key Indicator Sites

Appendix H. Descriptive Statistics for All Monitoring Stations Used in the Time-Series Study: Weekday Congestion Charging Hours

Appendix I. Results for Weekday Congestion Charging Hours

Appendix J. Descriptive Statistics for All Monitoring Stations Used in the Time-Series Study: Weekend (Congestion Charging Hours) Background Monitoring Stations Only

Appendix K. Results for Weekend Congestion Charging Hours: Background Monitoring Stations Only

Appendix L. The Use of Ethane as a Dispersion Indicator

Appendix M. Bivariate Polar Plot Analysis

ABOUT THE AUTHORS

Frank Kelly obtained his Ph.D. in 1982 and holds the chair in environmental health at King's College London where he is also head of the ERG and deputy director of the MRC-HPA Centre for Environment & Health. He has considerable experience in managing and coordinating interdisciplinary research in multicenter projects, including the HEI-funded CCS study and the Low Emission Zone baseline study. He contributes to the activities of a number of expert groups including U.K. government and WHO panels.

Ross Anderson is professor of epidemiology at the Centre for Epidemiology at St. George's, University of London. He has an international reputation as a leading researcher in the field of air pollution epidemiology, having a long track record of national and international research commitments. He is a member of the Expert Panel on Air Quality Standards (EPAQS) and the WHO Air Quality Expert Group. He was also a member of the U.S. National Academy of Science committee that reported on methods for estimating the health benefits of reducing ambient air pollution through regulations.

Ben Armstrong is an applied medical statistician at the London School of Hygiene & Tropical Medicine, with long-standing interest in the application of statistics to environmental health. He is a member of the Committee on the Medical Effects of Air Pollution (COMEAP) and the HEI Health Review Committee.

Richard Atkinson is a lecturer in statistics at St. George's, University of London, and has a special interest in the methods for quantifying the health impacts of outdoor air pollution. He is member of the COMEAP sub-committee set up to reevaluate the evidence for health effects of outdoor air pollution.

Ben Barratt has worked within the Air Quality Monitoring Team at the ERG, King's College London since 1994 and is currently deputy manager. His key skills lie in establishing and managing regional air quality monitoring networks and interpreting monitoring results through software systems development, internet reporting methods, and assessment intervention impacts.

Sean Beevers has more than 10 years of experience with air pollution measurement, and emissions and air pollution modeling at the ERG, King's College London. He has managed the emissions assessments for a number of large infrastructure projects in London and South East England as well as a number of key London developments including the London Atmospheric Emissions Inventory and the Congestion Charging Impacts Assessment.

Dick Derwent is director at rdscientific. He has considerable experience working with large data sets, extensive understanding of air quality issues in London, and a background in atmospheric science. He is a member of AQEG, EPAQS, and the WHO Air Quality Expert Group.

David Green manages the 16 monitoring sites within the LAQN that are affiliated with the AURN. In 1995, the ERG, King's College London, became the first Regional Management Unit of the (then) Automatic Urban Network. David managed the installation of the Marylebone Road site and is responsible for its operation. It is situated on the IRR (boundary of the CCZ) and gathers the most comprehensive set of air pollution data in the AURN. His research interests include methods for measuring airborne particles.

Ian Mudway leads the Lung Biology Group at King's College London and has 15 years of experience studying the oxidative basis of air pollution, initially focusing on the oxidative gases ozone and NO_2, but more recently addressing the toxicity of ambient and vehicle-derived particulates.

Paul Wilkinson is an environmental epidemiologist and public health physician at the London School of Hygiene & Tropical Medicine, with particular interest in environmental hazards to health, including climate change and outdoor air pollution. He is holder of a Public Health Career Scientist Award, which focuses on the methods of assessing quantitative public health impacts.

OTHER PUBLICATIONS RESULTING FROM THIS RESEARCH

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ABBREVIATIONS AND OTHER TERMS

AURN	Automatic Urban and Rural Network
CCH	congestion charging hours
CCS	congestion charging scheme
CCZ	congestion charge zone
CO	carbon monoxide
CO_2	carbon dioxide
CUSUM	cumulative sum
DEFRA	U.K. Department for Environment, Food and Rural Affairs
ERG	Environmental Research Group
GM	geometric mean
H & F	Hammersmith & Fulham [borough]
HGVs	heavy goods vehicles
K & C	Kensington & Chelsea [borough]
LAEI	London Atmospheric Emissions Inventory
LAPT	King's College London Air Pollution Toolkit
LAQN	London Air Quality Network
LET	King's College London Emissions Toolkit
LGVs	light goods vehicles
LT	London Transport
M25	M25 London Orbital Motorway
NO	nitric oxide
NO_2	nitrogen dioxide
NO_x	oxides of nitrogen
PM	particulate matter
$PM_{2.5}$	particles with an aerodynamic diameter ≤ 2.5 µm
PM_{10}	particles with an aerodynamic diameter ≤ 10 µm
RMS	root mean squared
SO_2	sulfur dioxide
SQL	structured query language
TEOM	tapered element oscillating microbalance
TfL	Transport for London
VOCs	volatile organic compounds
WHO	World Health Organization

The Impact of the Congestion Charging Scheme on Air Quality in London
Part 2. Analysis of the Oxidative Potential of Particulate Matter

Frank Kelly, H. Ross Anderson, Ben Armstrong, Richard Atkinson, Ben Barratt, Sean Beevers, Dick Derwent, David Green, Ian Mudway, and Paul Wilkinson

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ABSTRACT

There is growing scientific consensus that the ability of inhaled particulate matter (PM*) to elicit oxidative stress both at the air–lung interface and systemically might underpin many of the acute and chronic respiratory and cardiovascular responses observed in exposed populations. In the current study (which is part two of a two-part HEI study of a congestion charging scheme [CCS] introduced in London, United Kingdom, in 2003), we tested the hypothesis that the reduction in vehicle numbers and changes in traffic composition resulting from the introduction of the CCS would result in decreased concentrations of traffic-specific emissions, both from vehicle exhaust and other sources (brake wear and tire wear), and an associated reduction in the oxidative potential of PM with an aerodynamic diameter ≤ 10 µm (PM_{10}). To test this hypothesis, we obtained, extracted, and analyzed tapered element oscillating microbalance (TEOM) PM_{10} filters from six monitoring sites within, bordering, or outside the area of the congestion charging zone (CCZ) for the 3 years before and after the introduction of the scheme. In addition, from January 2005, TEOM PM_{10} filters were obtained from an additional 10 sites outside the zone in order to perform the first-ever assessment of within-city spatial variability in the oxidative potential of PM_{10}. Although London's PM_{10} was found to have remarkably high oxidative potential, it varied markedly between the studied sites, with evidence of increased potential at roadside locations compared with urban background locations. This difference appeared to reflect increased concentrations of copper (Cu), barium (Ba), and bioavailable iron (Fe) in PM_{10} collected at the roadside sites. PM_{10}'s oxidative potential after the introduction of the CCS did not change at the one urban background site within the zone. Yet compositional changes in PM_{10} were noted at the same site, including significant decreases in Cu and zinc (Zn) content, probably reflecting brake and tire wear (compared with increases in these metals at all sites outside the zone in the 3 years since the scheme's introduction). This pattern of results is consistent with observations of increased vehicle use throughout London in recent years and decreases in the number of vehicles entering the zone since the scheme's introduction.

INTRODUCTION

Although it is well established that a variety of acute and chronic health effects can be attributed to long-term exposures to elevated concentrations of ambient PM mass (Samet et al. 2000; Katsouyanni et al. 2001; Brunekreef and Holgate 2002; Janssen et al. 2002; Zanobetti et al. 2002; Bell et al. 2004), the mechanistic bases for these effects are less well understood. PM mass concentration has been used as a measure in the majority of epidemiologic studies, even though it overlooks PM's sources, constituents, and biologic activities. The potential importance of differences in PM components related to specific sources, such as traffic, is highlighted by cross-sectional studies that have shown associations between traffic-related air pollution and health effects using traffic density and proximity to

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This Investigators' Report is Part 2 of Health Effects Institute Research Report 155, which also includes *Part 1. Emissions Modeling and Analysis of Air Pollution Measurements*, a Commentary by the HEI Health Review Committee, and an HEI Statement about the research project. Correspondence concerning the Investigators' Report may be addressed to Professor Frank J. Kelly, Professor of Environmental Health, Environmental Research Group, MRC-HPA Centre for Environment & Health, School of Biomedical Sciences, King's College London, 150 Stamford Street, London SE1 9NH, U.K. Tel ++44 20 7848 4004; Fax ++44 20 7848 3891; frank.kelly@kcl.ac.uk.

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* A list of abbreviations and other terms appears at the end of the Investigators' Report.

busy roads as indicators of exposure (Delfino 2002; Janssen et al. 2003). The use of PM mass concentration as a measure is also challenging from a toxicologic perspective because much of the mass of PM_{10} (consisting of sodium chloride, crustal dust, ammonium sulfates, and nitrates) might be considered biologically inert, and the transition metals and organic chemical species found in PM_{10} at relatively low concentrations are likely to contribute significantly to its oxidative potential and subsequent toxicity. We therefore propose the use of alternative measures of PM toxicity as well as new PM metrics that are more relevant to its health effects (Künzli et al. 2006; Borm et al. 2007). One approach would require the identification of specific components of PM that could be mechanistically linked to human pathophysiology, specifically the induction of PM toxicity in biologic systems. However, others have argued that, owing to the chemical complexity of ambient PM, viewing ambient PM as a mixture of component mass contributions from different sources may be more fruitful, by simplifying the number of potential variables (Hopke et al. 2006; Ito et al. 2006, Mar et al. 2006). An alternative to either of these approaches is to study the ability of PM in aggregate to induce toxicity in biological systems and coupling this aggregate analysis with analysis of PM composition to provide the possibility of identifying key toxic components. This is the approach we have taken in this report.

There is growing scientific consensus that the ability of inhaled PM to elicit potentially damaging oxidative stress both at the air–lung interface and systemically might underpin many of the acute and chronic respiratory and cardiovascular responses observed in exposed populations (Gilliland et al. 1999; Nel et al. 2001; Li et al. 2002, 2003; Kelly 2003; Xia et al. 2004; Nel 2005). This ability to elicit oxidative stress has been linked to a number of PM characteristics, including its composition (Squadrito et al. 2001; Aust et al. 2002), size, and surface area (Brown et al. 2001). As shown in detail in Figure 1, inhaled PM elicits oxidative stress through various interrelated pathways — i.e., by direct introduction into the lung of oxidizing chemical species, such as redox-active transition metals (Aust et al. 2002) or quinones (Squadrito et al. 2001); by introduction of polyaromatic hydrocarbons (PAHs) that undergo biotransformation in vivo to quinones through the action of the cytochrome P450, epoxide hydrolase, and dihydrodiol dehydrogenase detoxification pathways (Bonvallot et al. 2001); and by stimulating inflammatory cells to undergo oxidative burst. The activation of inflammatory cells might be triggered by bacterial endotoxins on the surface of inhaled PM (Monn et al. 2003), futile phagocytic processing of PM (Soukup and Becker 2001), or by the upregulation of redox-sensitive transcription factors directing the synthesis of pro-inflammatory cytokines (Bonvallot et al. 2002).

Measuring the capacity of PM to oxidize physiologically relevant molecules in acellular models can therefore be used to provide a biologically relevant index of activity that effectively integrates PM composition, size, and surface area into a single biologically relevant metric of particle toxicity. Such an acellular model has previously been employed to address the oxidative potential of carbon black (CB) particles (used as a model of PM) (Zielinski et al. 1999), diesel exhaust PM_{10} (Mudway et al. 2004), PM with an aerodynamic diameter ≤ 2.5 µm ($PM_{2.5}$) from dung cake (Mudway et al. 2005b), and $PM_{2.5}$ from environmental tobacco smoke (Duggan et al. 2006), as well as ambient $PM_{2.5}$ (Künzli et al. 2006) and PM with aerodynamic diameters of 0.1 to 2.5 µm and 2.5 to 10 µm ($PM_{0.1-2.5}$ and $PM_{2.5-10}$, respectively) (Mudway et al. 2005a). It should be noted that this approach examines only the "intrinsic" oxidative potential of PM, reflecting the concentrations of redox-active metals, quinones, and radicals associated with the particle surface, not latent oxidative potential attributable to PAH metabolism or the induction of inflammation.

The introduction of the CCS in London provided a unique opportunity to examine the impact of traffic-management strategies on the oxidative potential of the PM_{10} in the city's airshed. We hypothesized that the reduction in vehicle numbers and changes in traffic composition observed after the introduction of the scheme would result in decreased concentrations of traffic-specific PM_{10} components derived both from vehicle exhaust and from other vehicular sources (such as brake and tire wear), with an associated reduction in PM_{10} oxidative potential. To test this hypothesis, we undertook a careful study of the characteristics and oxidative potential of PM_{10} collected on filters before and after the introduction of the CCS. TEOM PM_{10} filters were obtained from the six original sites within, bordering, or outside the area of the CCZ for the 3 years before and after the introduction of the scheme. Starting in January 2005, TEOM filters were also obtained from an additional 10 sites outside the zone to permit an assessment of the within-city spatial variability of PM_{10}'s oxidative potential.

This study represents the first substantial effort to investigate the effects of a major traffic intervention on the oxidative potential of ambient PM_{10} in a large city. In brief, significant spatial differences in oxidative potential were identified; PM_{10} samples collected from roadside sites had higher oxidative potential than those from urban background sites. Preliminary evidence suggested that the higher oxidative potential of the PM_{10} samples collected at

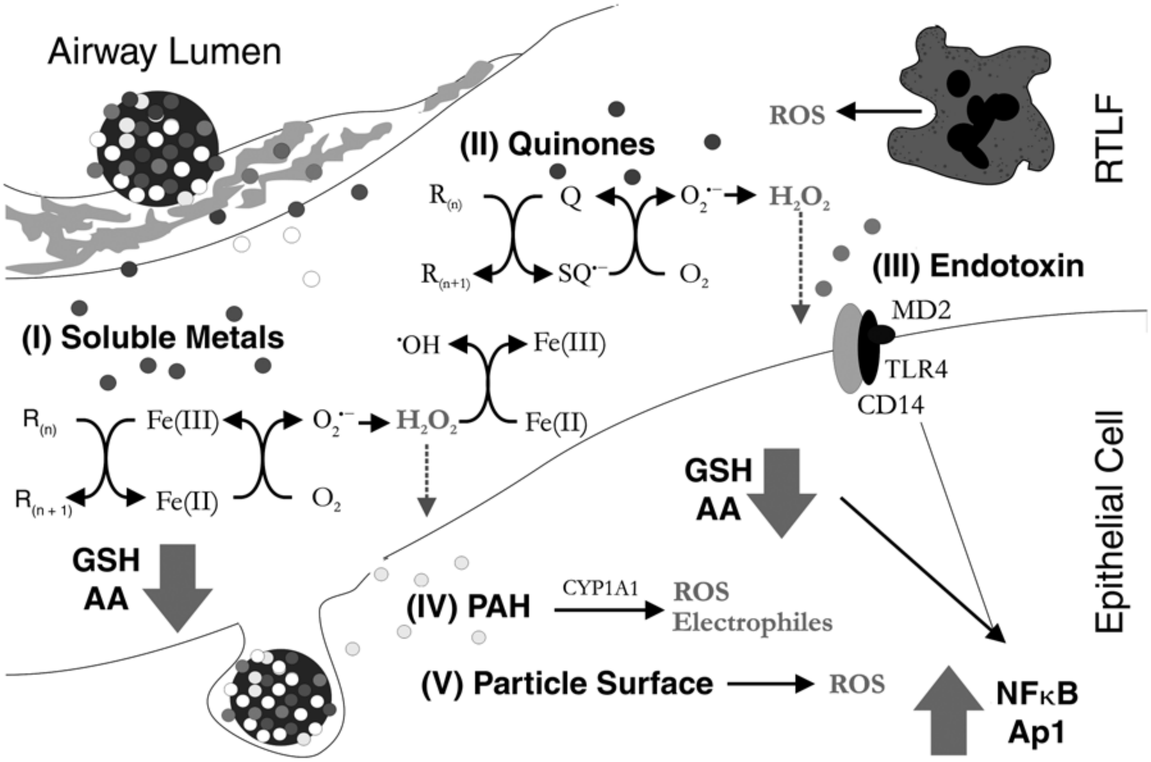

Figure 1. Pathways of particle-induced toxicity at the air–lung interface. Particles are purported to elicit oxidative stress through five interrelated mechanisms. (I) The introduction of redox-active aqueous metals, such as Fe, which redox cycles in the presence of biological reductants ($R_{(n)}$, where n represents the number of electrons) and oxygen to yield the superoxide radical ($O_2^{\bullet -}$), hydrogen peroxide (H_2O_2) and finally the damaging hydroxyl radical ($^{\bullet}OH$). (II) Quinones on the PM surface can also redox cycle in the presence of $R_{(n)}$ to form the semi-quinone radical ($SQ^{\bullet -}$) that also yields $O_2^{\bullet -}$ and H_2O_2. Both of these pathways will result in the loss of extracellular antioxidants and hence an altered extracellular redox environment. (III) Bacterial endotoxin, associated with the particle surface, has been shown to trigger inflammation through its interaction with the TLR4/CD14/MD2 receptor, which further adds to the oxidative burden in the airways. (IV) Polyaromatic hydrocarbons (PAHs) have no intrinsic oxidative activity themselves but will undergo biotransformations intracellularly through the action of cytochrome P450 1A1 (CYP1A1) to form reactive electrophiles and reactive oxygen species (ROS). (V) The particle surface itself has been shown to cause oxidative stress in vivo, though the mechanism by which this occurs is not well defined. Overall exposure to inhaled PM results in depletion of extra- and intra-cellular antioxidants, especially AA and GSH. This altered redox state results in the upregulation of redox-sensitive signaling pathways and transcription factors (NFκB and AP-1) leading to the increased production of cytokines and the development of airway inflammation.

the roadside was related to direct source emission from vehicle exhaust, tire wear, and brake wear. Experiments with selected metal chelators suggested that redox-active metals (Fe, Cu, nickel [Ni], and vanadium [V]) in the PM made major contributions to its observed oxidative potential; Cu, a component of brake pads, made particularly statistically significant contributions. It was notable that, although there were increases in the oxidative potential of PM resulting from increases in emissions from brake (Cu) and tire (Zn) wear throughout London over the 6 years of the study, the concentrations of these metals decreased at the one site within the zone, possibly reflecting the reduction of vehicle numbers within the zone. Despite this change in composition, the introduction of the CCS was not, upon analysis, found to lead to a reduction in the oxidative potential of the zone's PM. However, the analysis was hampered by the fact that filters from only one site within the zone were available and that there were substantial gaps in the filter archive from before the introduction of the scheme.

Although the current study has provided information on the relationship between traffic, PM composition, and the oxidative potential of PM_{10}, the fundamental question of the impact of traffic-management schemes on oxidative potential remains unanswered. However, important lessons and experiences have been gained over the course of the study, and these should prove invaluable for future studies in London and other cities around the world.

SPECIFIC AIMS

The primary goal of the current study was to determine if introduction of the CCS led to discernible changes in PM concentrations, composition, or oxidative characteristics. The secondary goal was to perform more comprehensive monitoring of sites within and outside of a proposed Western Extension of the zone in order to obtain robust baseline data to investigate the impacts of the extension on the above measures at a later date. These additional data also permitted an additional investigation of the spatial variability of the oxidative potential of PM_{10} in London.

The study had five specific aims:

1. To investigate the oxidative potential of ambient PM_{10} in London and to identify the PM_{10} components that affect this parameter;
2. To examine the impact of the CCS by comparing the oxidative potential of PM_{10} collected at designated indicator sites before and after introduction of the scheme;
3. To characterize spatial variation in the oxidative potential of PM_{10} within and outside the CCZ, especially for sites representative of urban background exposures and of roadside exposures;
4. To explore the contribution of motor vehicle emissions to the characteristics of ambient PM_{10} in London; and
5. To investigate whether volatile components lost from archived TEOM filters were likely to have resulted in an underestimation of oxidative potential.

METHODS

PM_{10} FILTER ARCHIVE

For the study of the impact of the CCZ, all historic (pre-2005) TEOM filters were obtained from an archive maintained by Bureau Veritas (Central Management and Control Unit for the U.K.'s Automatic Urban and Rural Network) or those LAQN sites funded by local authorities whose filters had already been collected by King's College London. Once the study began in 2005 provision was made for all subsequently collected TEOM PM_{10} filters to be sent directly to King's College London. To meet Specific Aim 2, filters were obtained for key urban background and roadside sites in and around the CCZ. (For a description of site characteristics, see the sidebar Air Monitoring Site Classifications in the London Air Quality Network on page 6 of Part 1.) These included a site within the zone (Bloomsbury—Russell Square, measuring the urban background), a site on the zone's boundary (Westminster—Marylebone Road, roadside), and filters from a number of control sites outside the zone (Haringey—Town Hall, roadside; Camden—Swiss Cottage, roadside; K & C—North Kensington, urban background; and Greenwich—Eltham, urban background). TEOM PM_{10} filters were requested from the archive to cover the period three years before the introduction of the scheme. In addition filters were obtained from an additional 10 sites, covering a wider geographic area, to permit an assessment of within-city spatial variability in the oxidative potential of PM_{10}. The geographic locations of the monitoring sites from which the TEOM filters were obtained are shown in Figure 2.

Since collection, the archived TEOM filters had been stored in sealed, non-opaque boxes at room temperature. Because of the intention to compare results from filters collected before and after the introduction of the CCS, it was decided to adopt the same storage procedure for the filters collected during the study. PM_{10} masses corresponding to each filter were calculated based on the exposure duration, TEOM flow rate, and the ambient PM_{10} concentration, and a randomized code was assigned using proprietary software developed by the investigative team at King's College London. The analyst responsible for the extraction of the filters and the subsequent analyses remained blind to the provenance of the samples for the duration of the study.

ANALYSIS OF OXIDATIVE POTENTIAL OF PM_{10}

To measure the oxidative potential of PM_{10}, we used an acellular model of respiratory tract lining fluid (RTLF) developed by Zielinski and colleagues (1999) and previously used to evaluate the toxicity of a variety of PM samples (Mudway et al. 2004, 2005b; Künzli et al. 2006). In this study, we further developed this protocol to analyze PM_{10} extracted from TEOM filters collected as part of London's program of air quality monitoring.

Extraction and Resuspension of TEOM Filter PM

Individual filters were placed in 50-mL conical-bottomed polypropylene tubes (Greiner Bio-One Ltd, Stonehouse, Gloucestershire, U.K.) with 2 mL of high-performance liquid chromatography (HPLC)–grade methanol (Sigma-Aldrich Chemical Co., Poole, U.K.). The tubes were then vortexed for 10 minutes before sonication using an ultrasonic disintegrator (model MSE Soniprep 150; MSE, London, U.K.) with a titanium probe at an amplitude of 5 microns for 30 seconds on ice. The methanol extract was decanted to a second tube and an additional 1 mL of methanol added to the filter remaining in the first extraction tube, which was then vortexed again for 10 minutes. The second methanol extract was then added to the first extract and dried under nitrogen

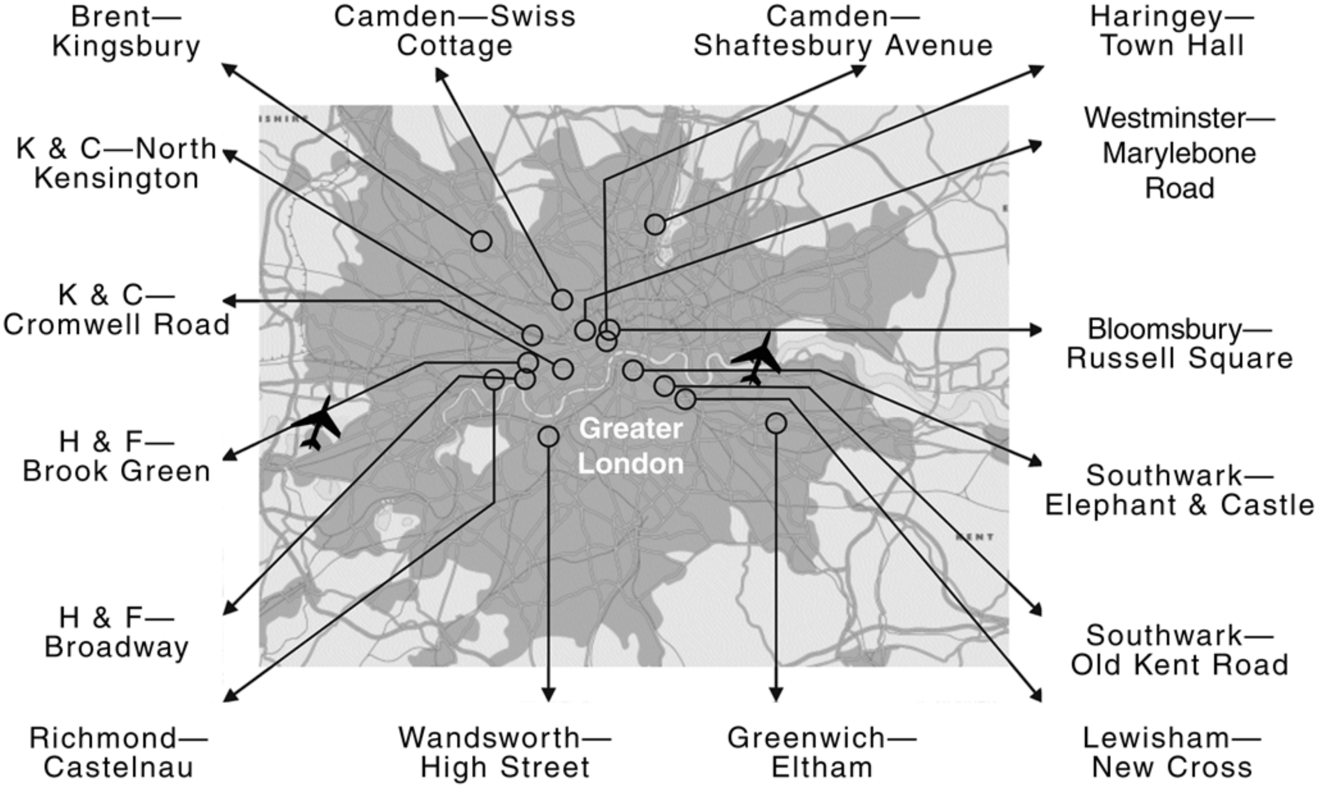

Figure 2. Map of Greater London illustrating the location of London Air Quality Network sites from which PM_{10} TEOM filters were obtained. For a detailed description of the location of each site, see Table 2.

at 37°C. The dried extract was subsequently resuspended in a purified 5% methanol solution (see details below) to a standard concentration of 15–1000 µg/mL (depending on the yield) by vortexing for 10 minutes and sonicating for 30 seconds at 15 microns. When oily extracts were obtained, which were not readily resuspended by vortexing, the residue was scraped from the sides of the extraction tubes into the resuspension solution using sterile plastic pipettes before sonication. Upon resuspension of the PM, samples were placed into a minimum of three aliquots and stored at −80°C until required for incubation in the synthetic RTLF model.

In most cases, the total PM mass assumed for each filter for the resuspension was the mass determined by the filter-loading data established from the TEOM measurements. When the PM_{10} mass for a filter was not known because of an error in TEOM operation (as happened at the Bloomsbury—Russell Square site from mid-August 2002 to June 2004), filter extractions were performed in preweighed Falcon tubes to permit an assessment of the actual extracted PM mass. Blank filters were also put through the same extraction procedure, and the mass of filter substrate dislodged from the blank filter surface was subtracted from the total mass recovered from the PM-loaded filters.

To make the purified 5% methanol solution (i.e., in which the concentration of contaminating metals was reduced), an ion-exchange resin (Chelex-100; Sigma-Aldrich Chemical Co.) was added (3 g per 100 mL solution) and stirred overnight at 4°C. The resin was removed by centrifugation (3,000 rpm for 15 minutes at 4°C), and the purified 5% methanol solution was carefully decanted. Before it was used in the resuspension protocol, its pH was adjusted to pH 7 using ion-exchange resin treated with 1 M HCl or 1 M sodium hydroxide. After PM samples were resuspended in the solution, the pH of the suspension was checked again and, when necessary, readjusted to pH 7 (as outlined above) before the samples were run through the incubation protocols.

Extraction and Resuspension of FDMS Filter PM

As outlined above, the majority of filters collected for this study were stored at room temperature to ensure comparability with the archived filters collected before the introduction of the CCS. However, there is a program to gradually replace TEOM with FDMS monitors across London. Because these monitors operate at lower capture temperatures it became feasible to consider the possible role of volatile components in driving PM oxidative potential. Therefore, to take advantage of this upgrade, in a small embedded study steps were taken to ensure that the volatile materials retained on the FDMS purge filter at 4°C were not lost during storage or filter processing. After collection, the FDMS filters were immediately transferred (on site) into Falcon tubes containing 20 mL chilled methanol. After sealing these tubes, the filters were transferred to King's College London in insulated containers, where they were stored at −20°C until extraction. Filter extraction was achieved by vortexing the filters in their methanol storage medium for 10 minutes. After this, the filters underwent probe sonication (5 micron amplitude) for 30 seconds on ice. The methanol extract was then transferred to a second Falcon tube, and an additional 10 mL of methanol were added to the filter in the first tube, which was then vortexed for an additional 10 minutes. Thereafter, the protocol was identical to that used for the TEOM filters, with the exception that the drying procedure was performed at a temperature below that at which the filters had been collected: 30°C for the base filters and 4°C for the purge filters. The PM extracts obtained from each of the filter types were then transferred to a −80°C freezer until required for analysis.

Examining the Relationship Between Measured and Calculated PM_{10} Masses on TEOM Filters To evaluate the efficiency of the extraction procedure, 50 TEOM PM_{10} filters underwent the extraction protocol described above using preweighed Falcon tubes. After the evaporation of methanol, the tubes were dried and weighed to obtain an extracted mass. In addition, before and after the standard extraction procedure, each filter was examined using low-vacuum scanning electron microscopy (Quanta FEG scanning electron microscope; FEI, Hillsboro, OR) in the King's College London Imaging Facility to examine the efficiency of the extraction and its potential impact on the integrity of the filter surface.

Measuring PM's Oxidative Potential

The oxidative potential of PM was determined using an assay based on a validated in vitro model of RTLF (Zielinski et al. 1999; Mudway et al. 2004). This model of synthetic RTLF consists of equimolar (200 µM) solutions of three antioxidants commonly found on the surface of the lung. It contains no lung tissue or cells. The assay was used to measure the ability of filter extracts to deplete antioxidants in the synthetic RTLF within a fixed period of time. Before exposures the concentrated PM suspensions were thawed at room temperature and diluted to 55.56 µg/mL. Incubations were then initiated by the addition of 50 µL of a concentrated RTLF (2 mM of ascorbate [AA], urate [UA], and reduced glutathione [GSH]) to 450 µL of the PM solutions at 55.56 µg/mL, to achieve final antioxidant concentrations of 200 µM and a PM concentration of 50 µg/mL. Co-incubations of PM and antioxidants were then performed in triplicate for 4 hours at 37°C at pH 7 in a Stuart Scientific Incubator (model S160; Keison Products, Chelmsford, Essex, U.K.), with gentle mixing. After the co-incubation period, the PM was removed by centrifugation (13,000 rpm for 1 hour at 4°C), and the remaining antioxidant concentrations were determined. To ensure intra-assay standardization between experiments, three control samples were also run with each batch (24 samples in triplicate): a particle-free control to quantify auto-oxidation, residual oil fly ash (ROFA) as a positive control, and carbon black (CB) particles (specifically M120 particles; Cabot, Billerica, MA, U.S.A.) served as a negative control. Detailed descriptions of the composition of these control particles have been published previously (Miller et al. 1998; Zielinski et al. 1999). All PM were analyzed in random order in a blinded fashion.

Ascorbate and Urate Analysis AA and UA concentrations were determined using reverse-phase high-pressure liquid chromatography with electrochemical detection in the amperometric mode (Iriyama et al. 1984). At the end of the incubation and after centrifugation of the samples, 50 µL of the reaction supernatant were removed and added to 450 µL of ice-cold metaphosphoric acid to achieve a final acid concentration of 5%. AA and UA concentrations were then determined simultaneously using reverse-phase HPLC with electrochemical detection. Aliquots (20 µL) of each sample were injected for analysis using an auto-sampler (model 234; Anachem, Luton, Bedfordshire, U.K.) onto a 10 × 300 mm 5-µM C18 column, eluted with 0.2 mM potassium phosphate buffer (K_2HPO_4–H_3PO_4), containing 0.25 mM octanesulfonic acid (pH 2.1) at a flow rate of 1 mL/min. An EG&G amperometric electrochemical detector (Jones Chromatography, Hengoed, Wales) was used for detection, with E set at 400 mV, a time constant of 5 seconds, cathodic output, and a sensitivity of 500 nA. Sample concentrations were determined against a standard curve of AA (0–25 µM) and uric acid (0–50 µM) prepared in 5% metaphosphoric acid.

Glutathione Analysis Reduced and oxidized glutathione were measured using the enzyme recycling method of Tietze modified for use on a plate reader (Baker et al. 1990). Aliquots (16.7 µL) of the reaction supernatants were then added to 983.3 µL 100 mM sodium phosphate buffer, pH 7.5, containing 1 mM EDTA. Standards containing 0–165 pmol/50 µL glutathione disulfide (GSSG), equivalent to 0–330 pmol/50 µL total glutathione (GSx), were also prepared in this buffer. Fifty µL of sample and standard were then transferred to the wells of a microtitre plate prior to the addition of 100 µL of a reaction mixture to achieve a final concentration in each well of 0.15 mM 5,5′-dithiobis-(2-nitrobenzoic acid) (DTNB), 0.2 mM nicotinamide adenine dinucleotide phosphate (NADPH), and 1 U of GSH reductase. Immediately after the addition of the reaction mixture, the microtitre plate was transferred to a plate reader (SpectraMAX 190; Molecular Devices UK Ltd., Wokingham, Berkshire, U.K.) for analysis. The rate of 5-thio-2-nitrobenzoic acid (TNB) formation was then measured by the rate of change of absorbance at 405 nm during a 2-minute period at 30°C. To determine GSSG concentrations, 5 µL of undiluted 2-vinyl pyridine (Aldrich Chemical Co., Poole, U.K.) were added to 130 µL of the samples and standards, vortexed for 5 seconds, and incubated at room temperature for 1 hour. Samples and standards were then plated out and run as above. The GSH pool was calculated indirectly by the subtraction of twice the GSSG concentration from the total GSx concentration.

Data Standardization and Quality Control To ensure that variations between sample batches in the RTLF assay were taken into account, all samples were run in parallel with the three PM controls described earlier: a particle-free control, a positive control (containing ROFA particles), and a negative control (containing CB). These controls as well as the stock antioxidant solutions were prepared in bulk at the start of the study for use throughout. The antioxidant concentrations of the stock solutions as well as the activity of the PM samples have been shown to be stable at −80°C for longer than 18 months. The data presented in these studies have been corrected for the known time-zero concentrations as well as the auto-oxidative loss of antioxidant occurring in the particle-free control during the 4-hour incubation. The positive and negative controls were used throughout the study as PM quality control samples. Full details of these data standardization procedures are outlined in Appendix C. PM Oxidative Potential Measurements.

Modifications to the RTLF Assays

Inhibitor Experiments To explore potential metal and nonmetal contributors to the observed oxidative activity, several inhibitor experiments were conducted using the RTLF assay outlined above. PM suspensions were co-incubated in the presence of a range of inhibitors, including the free-radical scavengers dimethylsulfoxide (DMSO, 4 mM stock concentration) and a mixture of Cu,Zn-superoxide dismutase (SOD) and catalase (CAT), prepared at a stock concentration of 3000 U/mL SOD and 1000 U/mL CAT. Metal dependence was investigated through the use of the transition-metal chelators diethylenetriamine pentaacetic acid (DTPA), ethylenediamine tetraacetic acid (EDTA), and desferroxamine mesylate (DES), all at stock concentrations of 4 mM. Experiments were performed by the addition of 25-µL aliquots of one of the above inhibitors to 425 µL of each PM suspension at a concentration of 58.8 µg/mL. Samples were pre-incubated at 37°C for 10 minutes before the addition of a 50-µL aliquot of the stock solution (2 mM) antioxidant solution, giving a final volume of 500 µL per reaction vessel and final concentrations of 200 µM AA, UA, and GSH; 50 µg/mL PM; 150 U/mL SOD, 50 U/mL CAT; and 200 µM DMSO, DTPA, EDTA, and DES. Samples were then incubated for 4 hours at 37°C with gentle vortexing, after which antioxidant concentrations were determined as outlined above.

Ascorbate Depletion Assay The oxidative potential of a number of representative PM samples (whose criteria for selection are discussed in the Results section) was also assessed by their capacity to deplete AA from an AA-only model. This approach was used to estimate the metal-dependent versus metal-independent oxidative potential of PM using the transition-metal chelator DTPA. PM suspensions were prepared as outlined above and were diluted to a starting concentration of 12.5 µg/mL before incubation with AA. All PM incubations were performed in triplicate in ultraviolet-transparent 96-well flat-bottomed microplates (model UV-Star; Greiner Bio-One Ltd., Stonehouse, Gloucestershire, U.K.). For the determination of total oxidative potential, incubations were initiated by the addition into each well of 20 µL of a concentrated stock of AA (2 mM) containing 160 µL of a PM suspension (12.5 µg/mL) and 20 µL of ultrapure resin-treated water after a 10-minute equilibration at 37°C in the plate reader. Metal-independent oxidation was estimated using a similar method beginning with the addition of 20 µL 2 mM AA stock to 160 µL PM suspension (12.5 µg/mL) but with 20 µL 4 mM DTPA instead of the ultrapure water.

After the incubation was initiated, the concentration of AA was monitored every 2 minutes for a period of 2 hours by measuring the absorbance at 265 nm. To control for the contribution of the absorbance of the PM itself, AA-free controls containing 40 µL ultrapure resin-treated water and 160 µL of individual PM stocks were run in parallel on the plate and subtracted from the sample absorbance readings. To control for the background absorbance in the chelator-treated samples, similar controls were also run containing 20 µL water and 20 µL 4 mM DTPA. The rate of AA depletion was determined by performing a linear regression for the initial segment of a concentration-versus-time plot using data analysis software (Origin, version 5.0; OriginLab Corp., Northampton, MA) for each of the triplicates; the rate of AA depletion was finally expressed as the mean nmol/sec ± standard deviation. Metal-dependent oxidation was calculated as the difference between the total and the metal-independent oxidative potential.

PM COMPONENTS AND CHARACTERISTICS THAT CONTRIBUTE TO OXIDATIVE POTENTIAL

In addition to measuring oxidative potential, each PM_{10} sample was assayed for a panel of metals (aluminum [Al], arsenic [As], Ba, beryllium [Be], cadmium [Cd], Cu, Fe, manganese [Mn], molybdenum [Mo], Ni, lead [Pb], V, and Zn) selected for their relationship to known traffic sources. The concentrations of individual metals were then related to the observed oxidative potential of PM_{10}. The selected metals are listed in Table 1 with reported source attributions and supporting references.

Table 1. Source Attribution of Selected Metals Found in PM

Potential PM Component / Source(s)	Reference(s)
Ba	
Lubricating oil	de Miguel et al. 1997
Brake wear	Harrison et al. 2003
Cd	
Diesel fuel	Onianwa 2001
Lubricating oil	Harrison et al. 2003
Brake wear	Weckwerth 2001
Carriage wear[a]	de Miguel et al. 1997
Cu	
Diesel fuel	Manoli et al. 2002
Lubricating oil	de Miguel et al. 1997
Brake wear	Weckwerth 2001, Harrison et al. 2003, Laschober et al. 2004
Fe	
Brake wear	Weckwerth 2001
Mo	
Diesel fuel	Harrison et al. 2003
Brake wear	Weckwerth 2001
Ni	
Diesel fuel	Weckwerth 2001
Lubricating oil	de Miguel et al. 1997
Pb	
Brake wear	Laschober et al. 2004, Weckwerth 2001
Zn	
Diesel fuel	Weckwerth 2001, Harrison et al. 2003
Lubricating oil	Laschober et al. 2004
Brake wear	Laschober et al. 2004
Carriage wear	Laschober et al. 2004
Tire wear	Weckwerth 2001, Harrison et al. 2003

[a] Wear on the body of the vehicle.

Inductively Coupled Plasma–Mass Spectrometry Analysis of Aqueous PM Extracts

In the current study, we wished to examine how the bioavailable metals in PM_{10} contributed to its measured oxidative potential. Because metal bioavailability is a function of the metals' solubility and the ligand environment (Aust et al. 2002), initial experiments were performed to establish which ligands to use and how to treat the samples. To examine the impact of various ligand environments on metal bioavailability, 12 triplicate samples of PM_{10} suspensions (50 µg/mL) derived from PM_{10} filters extracted as part of the ongoing study (from both roadside and urban background monitoring sites) were prepared in ultrapure resin-treated water, synthetic RTLF (containing 200 µM AA, UA, and GSH), AA (200 µM), or citrate (1 mM). The samples were then incubated for 4 hours at pH 7.0 and 37°C with gentle mixing. At the end of this period, the samples were pooled and centrifuged at 13,000 rpm for 1 hour at 4°C prior to 1 mL being passed through a 0.02-µm syringe filter (model Anotop 0.02 µm, Whatman, Kent, U.K.). A 0.5-mL portion of this combined supernatant was then added to 1.5 mL of ultrapure resin-treated water in non-colored 15-mL centrifuge tubes (Elkay Laboratory Products, Basingstoke, Hampshire, U.K.). All tubes and pipette tips were pre-washed in 5% nitric acid followed by ultrapure water before use. In addition to this experiment, the relationship between soluble-metal concentrations measured before and after a 4-hour incubation in ultrapure resin-treated water was also examined. Based on the findings of these preliminary studies (described in the Results section), all of the TEOM PM_{10} samples from the archived filters were analyzed for metals according to the following protocol.

One to two mL of each PM_{10} suspension (previously prepared) were centrifuged at 13,000 rpm for 1 hour (4°C) to remove particles. To ensure the removal of all particles, the resulting supernatant was filtered through a 0.02-µm syringe filter (model Anotop-0.02 µm, Whatman). A 0.9-mL portion of the filtrate was then added to 0.9 mL ultrapure resin-treated water before analysis by inductively coupled plasma mass spectrometry (ICP–MS). Samples were transferred to the Mass Spectroscopy Unit at King's College London for quantification of ^{27}Al (natural abundance 100%),

^{75}As (100%), ^{135}Ba (6.592%), ^{9}Be (100%), ^{111}Cd (12.8%), ^{63}Cu (69.15%), ^{56}Fe (91.72%), ^{55}Mn (100%), ^{95}Mo (15.92%), ^{60}Ni (26.223%), ^{208}Pb (52.4%), ^{50}V (0.25%), and ^{56}Zn (91.72%) using an ICP–MS (model ELAN DRC MSF008; Perkin-Elmer, Chalfont Road, Buckinghamshire, U.K.). The selected isotopes were chosen to avoid known potential isotopic interferences. The potential ArO^+ interference for ^{56}Fe, the major isotope of iron, was removed through its reaction with ammonia, using a dynamic reaction cell. Metal concentrations were determined with reference to a four-point standard curve based on an ICP multi-element standard solution (VI CertiPUR, Lot. No. OC529648; Merck Boulevard Industrial Park, Nottingham, U.K.). All concentrations were corrected for background metal concentrations determined in an ultrapure resin-treated water blank run in parallel with each batch of samples. Each batch (consisting of 80 to 120 samples) was also run in parallel with controls: a positive control (ROFA) and ambient $PM_{2.5–10}$ samples collected from London (extracts from both particle controls were taken from 150-µg/mL stock suspensions). The $PM_{2.5–10}$ sample was run to provide Fe and Cu measurements, because these metals were in low abundance in the aqueous ROFA extract. These controls, plus one of the dilutions of the certified multi-elemental standard, were interspersed at set intervals throughout the experimental run to provide information on the potential drift in instrument sensitivity over time. All digestion vessels and pipette tips that came into contact with the PM samples were acid-washed in 2% nitric acid before use.

Determination of Surface-Mobilizable Fe and Cu Concentrations

Much of the current literature examining PM metal toxicity often erroneously equates their aqueous metal content with the biologically active pool. The situation in vivo is not so simple with the release of metals from the particle surface strongly influenced both by the pH and the ligand environment of the cell or the extracellular compartment (Aust et al. 2002). These ligands, which range from low-molecular-weight species such as citrate to high-molecular-weight chelator proteins such as transferrin, have the capacity to “mobilize” metal pools from the PM surface and thus strongly influence their bioavailability. To attempt to obtain a more informative estimate of bioavailable Fe and Cu we made use of the chromogentic chelators bathophenanthroline disulfonate (BPS) and bathocuproine disulfonic acid (BCS), respectively. These chelators have affinities for Fe and Cu that are similar to the affinities of many of the major biological ligands in vivo.

Total (Fe^{2+} and Fe^{3+}) iron concentrations were measured in all of the PM_{10} extracts from TEOM filters collected at each of the 16 sites (from January 2005 to April 2006) using the chromogenic iron-chelator BPS. BPS binds to ferrous iron, forming a complex that absorbs strongly at 535 nm (Nilsson et al. 2002). This characteristic allows for the determination of total iron following reduction with an excess of AA. Briefly, a 245-µL sample of PM suspension (55.56 µg/mL) was treated with 12.5 µL 200 mM AA and 5 µL of a stock 50 mM BPS solution. This mixture was then incubated for 30 minutes at room temperature in the dark. The samples were then centrifuged at 13,000 rpm for 10 minutes at 4°C, after which 200 µL of the supernatant were transferred to a 96-well plate, and the absorbance was read at 535 nm using a plate reader. Parallel particle blanks were made by adding 5 µL ultrapure resin-treated water instead of the BPS to 245 µL of the PM suspension and 12.5 µL AA and taking them through the same steps as the samples. The resulting blank values were then subtracted from the total values before the concentrations were calculated from the slope of the relevant standard curve (0.1–50 µM ferrous ammonium sulfate).

Total copper concentrations (Cu^+ and Cu^{2+}) were measured in PM suspensions using the chromogenic chelator BCS. Five µL BCS (50 mM) and 12.5 µL AA (20 mM, pH 7) were added to 245 µL of the standard (0.1–50 mM) or the sample (55.56 µg/mL) before a 30-minute incubation at room temperature in the dark. Parallel PM blanks, in which the BCS was replaced with 5 µL ultrapure resin-treated water, were also prepared and incubated as above. Samples, standards, and blanks were then passed through a 0.02-µm syringe filter, and 200 µL of the resultant filtrate were transferred to a 96-well plate for determination of total copper concentration by absorbance at 438 nm.

MODELING OF VEHICLE CONTRIBUTIONS TO PRIMARY PM_{10}

An analysis was conducted to provide insight to possible source contributions to the PM_{10} in London, with a focus on contributions to primary PM_{10} from vehicular emissions. It involved a comparison between modeled estimates of primary PM_{10} mass and measured primary PM_{10} mass from monitors at the 16 monitoring sites in London that were the subject of the main study.

Contributions to primary PM_{10} mass from vehicular sources were estimated first by modeling exhaust, tire wear, and brake wear emissions associated with road transport using methods consistent with COPERT III, a computer software program. A brief description of the program can be found in Appendix D, with full details available in the COPERT III’s user manual (see Ntziachristos and Boulter 2003). Emissions of each component of primary PM_{10} were then used with air-dispersion models to create a concentration surface across London. At the selected monitoring site locations, the projected mass of PM_{10} from exhaust, tire wear, and brake wear were summed to provide the estimate of total modeled primary PM_{10}, with each mass expressed as gravimetric-equivalent values.

Receptor analysis was also used to estimate primary PM_{10} using NO_x tracer approach as detailed in Fuller and Green (2006). There was good agreement (see Table 6 later in this report) with the modeled sum of PM_{10} from exhaust, tire wear, and brake wear from selected monitoring sites in rural areas outside of London.

ANALYTIC APPROACH

Data Sets

Our approach to analysis of the relationship between PM and oxidative potential followed the broad objectives outlined in the Specific Aims section and thus relied on differing groups of data and types of analyses. In the first set of analyses, the entire data set was used (including all sites and the full duration of the study, for a total of approximately 730 filters [Table 2]). We explored the relationship between the different measures of PM's oxidative potential (comparing oxidative potentials based on AA or GSH depletion expressed either per unit mass (μg PM) or per m^3 of

Table 2. Details of the 16 London Air Quality Network Monitoring Sites Used in Study

Site	Code	Classification	Site Location	Filter Archive Collection Period (Start Date–End Date)	Filters[a] (*n*)
Bloomsbury—Russell Square	BL0	Urban background	Within the CCZ	3/21/2001–3/16/2006	71
Westminster—Marylebone Road	MY1	Roadside	CCZ boundary	11/15/2000–3/29/2006	212
Camden—Swiss Cottage	CD1	Roadside	Outside the CCZ	12/14/1999–3/9/2006	71
Haringey—Town Hall	HG1	Roadside	Outside the CCZ	12/14/1999–3/6/2006	87
K & C—North Kensington	KC1	Urban background	Outside the CCZ	1/9/2002–3/13/2006	31
Greenwich—Eltham	GR4	Urban background	Outside the CCZ	1/31/2000–3/17/2006	65
Brent—Kingsbury	BT1	Urban background	Outside the CCZ and Western Extension	7/15/1999–3/22/2006	13
Camden—Shaftesbury Avenue	CD3	Roadside	Within the CCZ	1/9/2005–11/30/2005	11
K & C—Cromwell Road	KC2	Roadside	Within Western Extension to the CCZ	9/7/2004–9/26/2005	28
Southwark—Elephant & Castle	SK1	Urban background	Outside the CCZ and Western Extension	1/13/2004–3/30/2006	18
Southwark—Old Kent Road	SK2	Roadside	Outside the CCZ and Western Extension	1/6/2004–3/30/2006	28
Lewisham—New Cross	LW2	Roadside	Outside the CCZ and Western Extension	1/20/2005–3/23/2006	12
H & F—Broadway	HF1	Roadside	Outside the CCZ and Western Extension	9/29/2004–3/15/2006	32
H & F—Brook Green	HF2	Urban background	Outside the CCZ and Western Extension	9/27/2004–3/15/2006	13
Richmond—Castelnau	RI1	Roadside	Outside the CCZ and Western Extension	8/23/2004–3/23/2006	20
Wandsworth—High Street	WA4	Roadside	Outside the CCZ and Western Extension	11/8/2004–5/24/2005	17

[a] Approximately 730 PM_{10} samples were analyzed in a blinded fashion. Upon unblinding the sample codes it was apparent that three of the samples had collection periods that overlapped with other samples. After reviewing the data it was decided that this reflected labeling errors by the site operators and these samples were excluded from all subsequent analyses.

air. Further, we explored the relationship between measures of PM's oxidative potential and its metal or elemental composition and at selected sites and when available, meteorologic variables and copollutant concentrations.

In the second set of analyses, the impact of the CCS on PM's oxidative potential and composition (i.e., Specific Aim 2) was assessed using archived filters collected from roadside and background sites adjacent to and outside the CCZ (Bloomsbury—Russell Square, Westminster—Marylebone Road, Camden—Swiss Cottage, K & C—North Kensington, Haringey—Town Hall, and Greenwich—Eltham; see Table 2 for details) during the 3 years before and the 3 years after the introduction of the scheme.

In the third set of analyses, within-city spatial variability of PM's oxidative potential and composition was examined (i.e., Specific Aim 3). The analysis included data from sites designated for the evaluation of the impact of the introduction of the CCZ's Western Extension, on February 16, 2006. It therefore included data collected from 16 sites (i.e., the sites in the second set of analyses plus Brent—Kingsbury, Camden—Shaftesbury Avenue, H & F—Broadway, H & F—Brook Green, K & C—Cromwell Road, Lewisham—New Cross, Richmond—Castelnau, Southwark—Elephant & Castle, Southwark—Old Kent Road, and Wandsworth—High Street; described in Table 2) during the period of the HEI contract (January 2005–April 2006). In addition to comparing PM's oxidative potential and composition across all the sites, site-specific relationships between PM's oxidative potential and composition were also evaluated. The sites selected for this evaluation were ones where the contrasts between oxidative potential measured were greatest (i.e., they had high or low oxidative potential). At each site the contributions of bioavailable Fe and Cu were examined through the use of free-radical scavengers and metal chelators. The sites were further classified as roadside or urban background sites. In the fourth set of analyses, addressing Specific Aim 4, the chemical and oxidative potential measurements and compositional data of the PM_{10} samples were brought together with the modeling approaches designed to assess the potential contributions of vehicle exhaust, tire wear, and brake wear emissions to the PM_{10} concentrations measured at selected sites. Because the model was run using data from 2005, only the compositional and oxidative potential measurements for this year were included in this analysis.

The final set of analyses examined whether loss of volatile components from the TEOM filters, due to the heated air inlet, resulted in artifactual losses of oxidative components. This was achieved by comparing PM_{10} from filters obtained from TEOM and FDMS instruments operated in parallel at a roadside site and an urban background site in London. These analyses addressed Specific Aim 5 and consisted of the analyses of PM_{10} extracted from filters collected at 50°C (TEOM) as well as at 30°C and 4°C (FDMS).

Statistical Analysis

Descriptive data on oxidative potential and aqueous metal concentrations (approximately 730 filters) are summarized in Appendix C, Table C.1, together with information on their statistical distributions. For the purposes of accepting data as normally distributed, the values of skewness and kurtosis were required to be less than 1. Using these criteria as well as normality plots (made using SPSS 14.0 statistical software; IBM, Feltham, Middlesex, U.K.), all measures of oxidative potential were found to be normally distributed and hence are described throughout the report by their mean values with standard deviations.

Table C.1 shows that metal concentration data did not satisfactorily meet the conditions of normality despite using a range of normalization procedures; hence they are described throughout as medians with interquartile ranges, with comparisons of median values performed using the nonparametric Mann–Whitney U and Kruskal–Wallis tests. Copollutant concentrations (nitric oxide [NO], nitrogen oxides [NO_x], nitrogen dioxide [NO_2], carbon monoxide [CO], sulfur dioxide [SO_2], ozone [O_3], and PM_{10}) as well as site temperature were also available at many of the selected sites and were also generally (but not always, see for example CO and SO_2) found to be normally distributed. Descriptive data for these variables are summarized in Table C.2.

The significance of variation of means across the monitoring sites was tested by analysis of variance (ANOVA), using the Games–Howell test to provide robustness against unequal within-site variances, given different sample sizes (i.e., the number of filters collected) for each site. The significance of associations between all measured numerical variables (PM composition, oxidative potential, and copollutant concentrations) was assessed using Pearson correlation when both components were normally distributed or the Spearman rank order test when one or both of the components were non-normally distributed.

Multiple linear regressions with a backward deletion approach were used to determine the associations between the various measures of oxidative potential with PM metals and copollutant concentrations. Some analyses were carried out on all filters, some were restricted to filters from one monitoring site (referred to as within-site analyses), and some were carried out on the means of data from filters collected from each monitoring site ($n = 16$).

Because of likely clustering of the approximately 730 data points by monitoring site, the all-data analyses described above are likely to have yielded spuriously small P values.

Therefore, when significance levels are given for these analyses, they are not emphasized. Because of temporal autocorrelation, the within-site analyses (e.g., for associations between metals and oxidative activity) are also subject to spuriously small *P* values, although probably less so than the all-data analyses. We are nevertheless cautious in interpreting all *P* values other than those based on the means from each of the 16 sites. For this reason, naïve analyses for all data and within-site data are described only in Appendix E, to permit comparison with previous studies in which similar approaches have been adopted. Additional analyses were performed to test the sensitivity of key results to the clustering of data by sites and to possible temporal auto-correlation within sites.

RESULTS

CHARACTERIZATION OF THE OXIDATIVE POTENTIAL OF PM_{10}

Before characterizing the oxidative potential of PM_{10}, experiments were conducted to determine whether calculated mass was predictive of the extracted mass. In the experiments outlined in this report, PM_{10} was extracted from filters and resuspended to the desired concentration based on the masses predicted by the TEOM (or FDMS). To examine the relationship between the predicted mass of PM_{10} on the TEOM filters and the measured mass after PM extraction, 50 randomly selected filters were weighed after extraction. Comparison of the two masses, shown in Figure 3, showed an association between the predicted and weighed masses ($R = 0.46$), which improved markedly when four of the outlying values were removed ($R = 0.72$). Although removal of the outliers suggests a reasonable association between the predicted and weighed masses, inspection of the data in relation to the line of identity suggests that the weighed mass was generally in excess of the predicted value, implying a contribution to the measured mass from the filter matrix.

To investigate whether the filter matrix was likely to be contributing to the measured mass, PM filter surfaces both before and after extraction were examined using scanning electron microscopy. Figure 4 shows scanning electron micrographs of TEOM PM_{10} filters, both loaded with PM_{10} and after PM_{10} extraction, at increasing magnifications (from 150 to 100,000 times). The high-magnification micrographs support the contention that PM of all sizes was removed effectively from the filter with little discernible disruption of the filter matrix. These micrographs supported the use of the predicted mass from the monitors as the measure of filter loading. Similar high-magnification scanning electron micrographs of FDMS filters before and after extraction are shown in Figure C.1.

Having decided to use mass predicted by the monitors, we extracted approximately 730 TEOM filters and assessed the oxidative potential of the recovered PM by analyzing its capacity to deplete AA, UA, and GSH from the synthetic RTLF over a 4-hour incubation period (37°C, pH 7). These raw data are shown in Figure C.2 and Figure C.3 in the batch order in which the samples were run. The figures also compare the antioxidant concentrations remaining in the samples to those in the particle-free control before and after the 4-hour incubation period, the positive control, the negative control, and a filter blank. The control values shown in Figures C.2 and C.3 represent mean concentrations averaged across the controls for the 33 filter batches analyzed in this study.

These data demonstrate that the capacity of PM_{10} to deplete antioxidants varied markedly on an equal-mass basis (50 µg/mL), ranging from samples that caused a complete depletion of AA over the 4-hour incubation period to samples that caused negligible depletion compared with the particle-free control. It was also apparent that a significant proportion of the PM extracts examined displayed more oxidative potential than an equal concentration of ROFA, the particle used in the positive control. No significant depletion of UA was seen in any of the samples examined (Figure C.2).

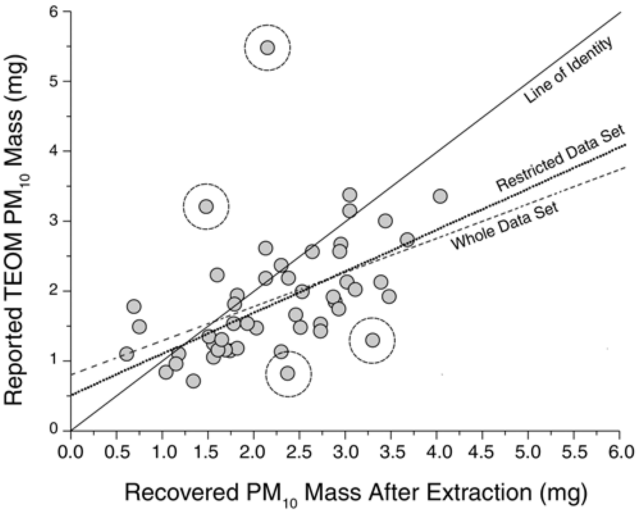

Figure 3. The relationship between reported TEOM mass and recovered mass in 50 randomly selected PM_{10} TEOM filters. The degree of association is illustrated relative to the line of identity. Lines of regression are shown for the whole data set and for the restricted data set after the four encircled data points were removed from the analysis. $R = 0.46$ with $P < 0.001$ for the regressions of the whole data set. $R = 0.72$ with $P < 0.0001$ for the regressions of the restricted data set.

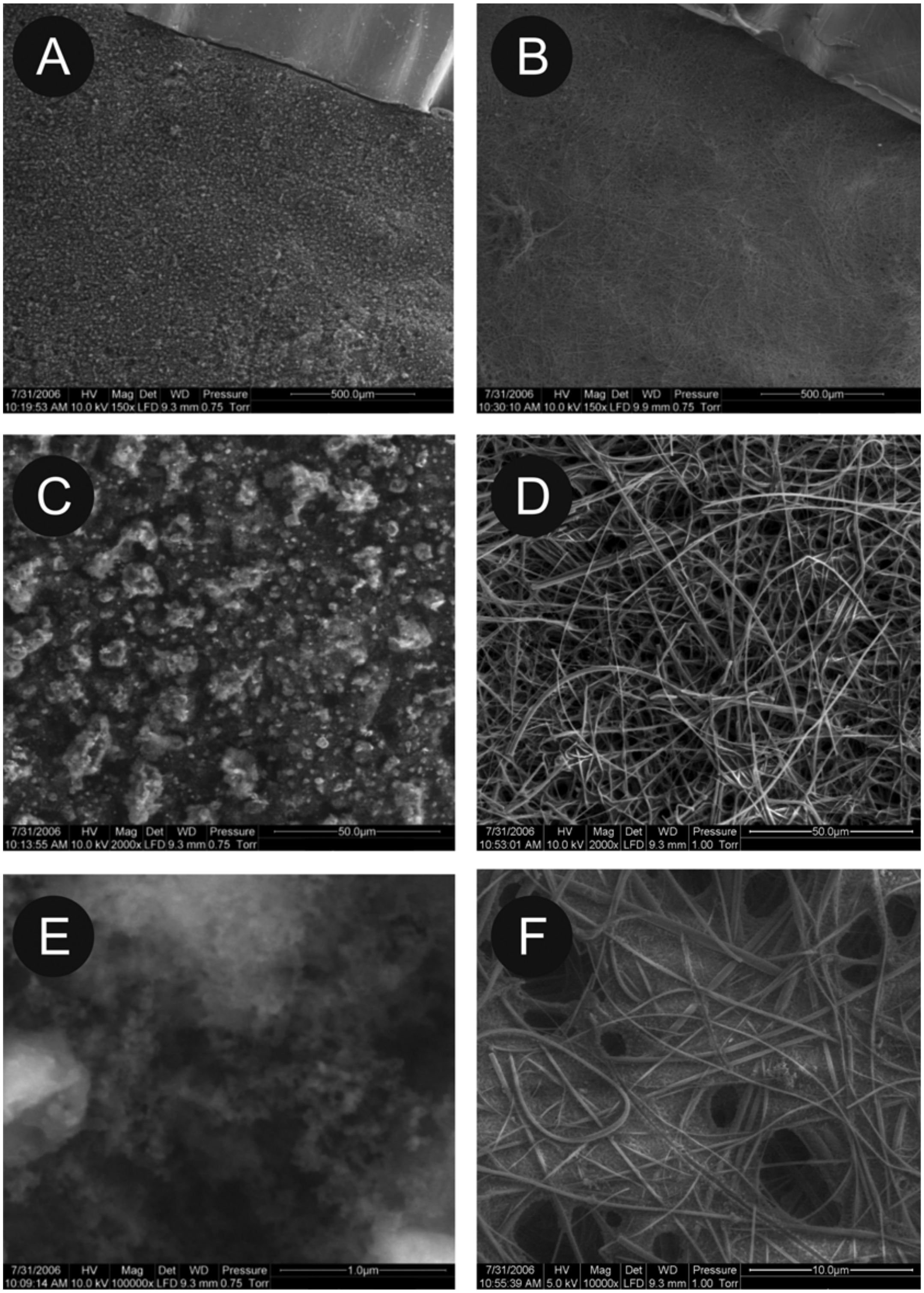

Figure 4. Scanning electron micrographs of TEOM PM_{10} filters from two monitoring sites. Panels **A, C,** and **E** are micrographs of filters collected from the Westminster—Marylebone Road roadside site (from October 17 to 24, 2001) before PM extraction. Panels **B, D,** and **E** are micrographs of filters collected from the Haringey—Town Hall roadside site (from February 8 to 18, 2002) after PM extraction. Original magnifications: **A,** 150×; **B,** 150×; **C,** 2000×; **D,** 2000×; **E,** 100,000×; and **F,** 10,000×.

The concentrations of GSx, GSSG, and GSH after the 4-hour incubation are shown in Figure C.3. A small, variable depletion of GSx was seen in a large proportion of the PM samples examined. Because these incubation conditions did not promote the oxidation of GSH to GSSG, the data imply either limited adsorption of GSH onto the particle surface or conjugation to organics. Again, the capacity of the PM samples to oxidize GSH to GSSG varied markedly. In contrast with the results for AA, no depletion of GSH was observed for the positive control, suggesting that the principal metal components of PM (Ni, V, and Zn) did not target GSH in the RTLF assay.

To present the oxidative potential of PM extracts in a more generally useful form, the data were expressed as a percentage of antioxidant depletion per µg of PM_{10}, relative to the particle-free control (assuming a linear dose–response relationship). A metric was thus derived for oxidative potential, scalable from 0 to 2. The terms OP^{AA} and OP^{GSH} indicate the oxidative potential represented by the capacity of PM to deplete AA or GSH, respectively. Only a weak association was observed between OP^{AA} and OP^{GSH}, indicating that AA and GSH varied in their response to different pro-oxidants (Figure C.4). Furthermore, no association was observed between the extent of AA and GSH depletion from the synthetic RTLF and the PM_{10} extracts expressed per unit mass, with the corresponding ambient PM_{10} concentration (Figure 5). Only a weak association was observed between OP^{GSH} and ambient PM_{10} (Figure 5). The latter results suggest that oxidative potential is not just a surrogate for ambient PM concentrations.

Having derived metrics for the oxidative potential of PM (expressed per µg PM_{10}) and demonstrated that they were not simply surrogates for ambient PM_{10} concentrations, we next derived similar metrics for OP^{AA} and OP^{GSH} expressed as PM_{10} per m^3 of ambient air. These four new metrics are illustrated in Figure 6 for approximately 730 filters, grouped by site, together with the corresponding ambient PM_{10} concentrations.

The formulation of these metrics was built upon the assumption of a linear relationship between the concentration of particulate and the rate of antioxidant depletion. However, it should be noted that catalytic metals (Ayres et al. 2008), quinones (Roginsky et al. 1999), and CB particles (Zielinski et al. 1999) have been shown to oxidize AA and other low-molecular-weight antioxidants in a near-linear, dose-dependent manner.

To investigate determinants of the oxidative potential of PM, a number of metals (Al, As, Ba, Be, Cd, Cu, Fe, Mn, Mo, Ni, Pb, V, and Zn) were examined in the PM extracts derived from the PM_{10} filters. Initially, the effect of the PM ligand environment on metal bioavailability was investigated by examining the concentrations of the metals after a 4-hour incubation in either water, 200 µM AA, synthetic RTLF, or 1 mM citrate. In all cases, the ligand environment was maintained at pH 7. Consistent with earlier reports, incubating particles in citrate was found to significantly elevate aqueous Fe concentrations (Aust et al. 2002) compared with incubation in water, AA, or synthetic RTLF (Figure C.5). Indeed, incubating particles in citrate resulted in a significant increase in concentrations of all the measured metals, with the exception of Pb.

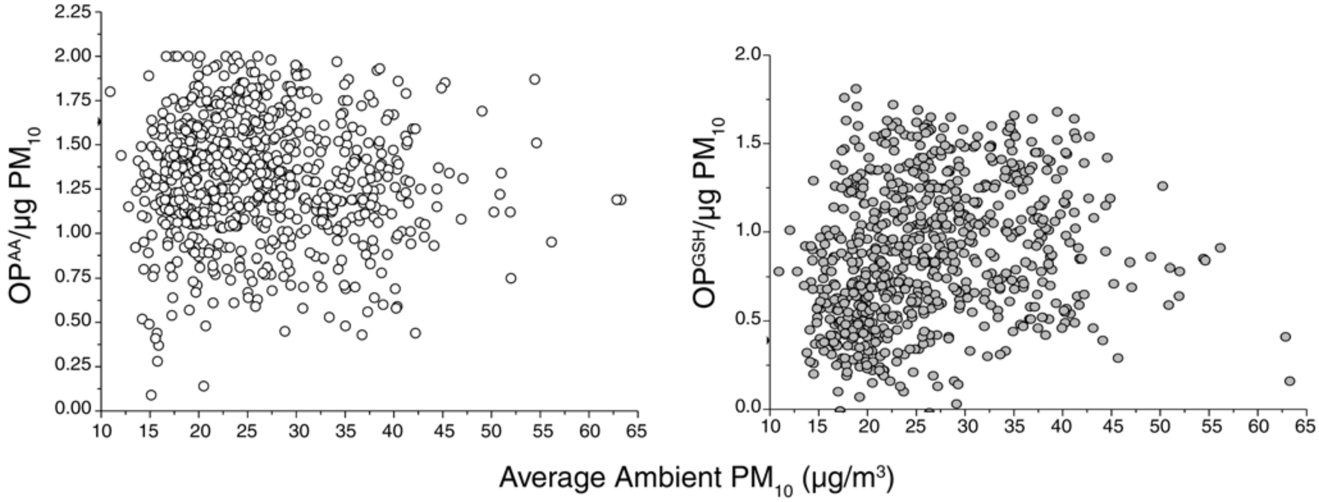

Figure 5. The association between OP^{AA} and OP^{GSH} per µg PM_{10} and the average ambient PM_{10} concentration observed at the sampled sites. No association was seen for OP^{AA}/µg. A weak but statistically significant association was noted for OP^{GSH}/µg ($r^2 = 0.05$, $P < 0.0001$, $n = \sim 730$).

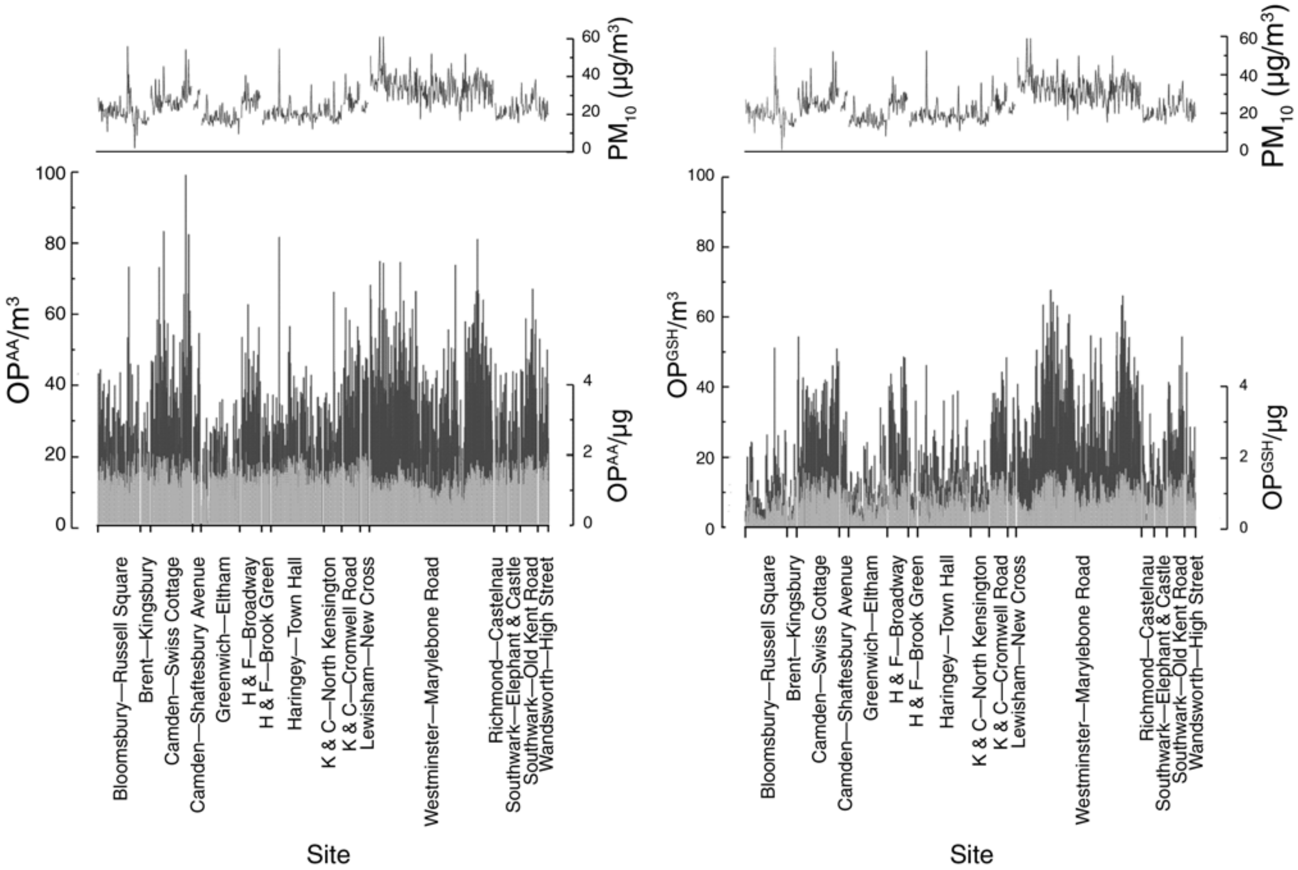

Figure 6. Comparison of two metrics of PM$_{10}$ oxidative potential for all the filter extracts used in the current study (n = ~ 730). The left-hand panel illustrates OP^{AA} expressed per μg PM$_{10}$ (light gray traces) or per m^3 air (black traces). The right-hand panel shows the equivalent data for OP^{GSH}. The upper panels show the ambient PM$_{10}$ concentrations covering each of the sampling intervals.

In general, the mobilization of the metals examined in the various ligand environments fell into three broad categories. In the first category, Cu and Zn concentrations (mean ± 1 standard deviation) were significantly increased after incubation in AA (88.9 ± 66.7 ng Cu/mg PM for incubation in water vs. 141.4 ± 77.3 ng Cu/mg PM for incubation in AA; 31.8 ± 22.2 ng Zn/mg PM for incubation in water vs. 50.4 ± 22.6 ng Zn/mg PM for incubation in AA), but this AA-dependent mobilization did not occur for Cu and Zn after incubation in synthetic RTLF (79.2 ± 41.2 ng Cu/mg PM and 43.1 ± 21.3 ng Zn/mg PM). In the second category, AA mobilized Al and Ni; co-incubation with UA and GSH did not block this mobilization (not shown in figure). In the third category, neither AA nor the complete antioxidant mixture increased aqueous concentrations of Mn, Fe, Pb, or V compared with water only. It was notable that, although the metals interacted in the ligand environment in various ways, strong Spearman correlations were observed between the concentrations of all the metals (except Al) in water and the concentrations in AA, synthetic RTLF, and citrate.

The temporal pattern of release of the same metals from particles over the 4-hour incubation period was also examined. With the exception of Mn, Ba, and Pb, all soluble-metal concentrations increased over the incubation period (Figure C.6). Although metals were clearly leaching into the synthetic RTLF over time, moderate to high Spearman correlations were observed between the metal concentrations at the beginning and end of the incubation period: Al ($r = 0.38$), As ($r = 0.99$, $P < 0.0001$), Ba ($r = 0.75$, $P < 0.0001$), Cu ($r = 0.35$), Fe ($r = 0.90$), Mn ($r = 0.98$, $P < 0.05$), Mo ($r = 0.96$), Ni ($r = 0.78$, $P < 0.0001$), Pb ($r = 0.81$, $P < 0.0001$), V ($r = 0.99$, $P < 0.0001$), and Zn ($r = 0.53$, $P < 0.001$).

Because little difference was apparent between metal concentrations observed after incubation in water and after incubation in synthetic RTLF (with the exception of Al and Ni), it was decided to examine aqueous metal concentrations in all filter extracts. Of the approximately 730 filters collected for the study, about 729 underwent ICP–MS (the sample from one filter had insufficient volume for this analysis); the raw results are summarized in Figure C.7. Although Cd, Be, and Mo were present at trace concentrations in a fraction of the samples, a large proportion of the samples yielded zero or negative values after subtraction of the blank concentrations. These metals were therefore omitted from subsequent analyses.

To establish how the metals and other copollutants influenced the oxidative potential of PM, a series of correlation analyses were performed using the entire data set. Because the metal data were non-parametric, the analyses were performed using the Spearman rank-order correlation. Table C.3 summarizes the correlations between OP^{AA} or OP^{GSH} (per µg) and metal concentrations, both for all sites and within each site. For all sites (with the substantial caveat that clustering by site strongly influences the strength of the associations seen), OP^{AA}/µg was most strongly associated with Fe, V, and Cu (correlations of 0.457, 0.374, and 0.304, respectively). There were weaker associations with As, Ni, Pb, and Zn. The strongest associations for OP^{GSH}/µg were with As and Ba (correlations of 0.212 and 0.263, respectively); there was a weaker association with Cu.

The correlation analyses with copollutant concentrations were performed using the metric of OP/m^3 and are summarized in Table C.4, both for all sites and within each site. Both OP^{AA} and OP^{GSH} were strongly associated with NO_x; associations with PM_{10} and $PM_{2.5}$ would be expected, because the OP/m^3 metric is adjusted for ambient PM_{10} mass concentrations. However, it was notable that OP^{GSH}/m^3 was more strongly associated with NO_x than was OP^{AA}/m^3, whereas the opposite was true for the metrics' associations with PM_{10} and $PM_{2.5}$. Although there was no association between OP^{AA} and CO, OP^{GSH} was significantly associated with CO.

To explore the relationship between the oxidative potential and PM_{10} composition further, multiple linear regressions were performed. A backward deletion approach was adopted for each oxidative potential metric, focusing on the metals with which the oxidative potential metrics had significant positive associations, based on the results of the Spearman correlations summarized in Table C.3. In this table, the degree of significance for each of the correlations is given only for individual sites; they are not provided for the all-site correlations (about 730 filters), because of the risk of inflated significance caused by autocorrelation in the data. For OP^{AA}/µg, the following metals were used in the regression modeling: As, Cu, Fe, Mn, Ni, Pb, V, and Zn, because in each case moderate positive correlations were noted across the combined sites. For OP^{GSH}/µg, Al, As, Ba, Cu, Fe, Mn, Ni, Pb, and V were used, although of these only As, Ba, Cu, and Mn were positively associated with OP^{GSH}/µg. The regression analysis revealed that the best model for predicting OP^{AA}/µg included aqueous As, Cu, Fe, Mn, Ni, Pb, V, and Zn concentrations, yielding an adjusted R^2 value of only 0.269; the largest standardized beta coefficients observed were for Fe (0.393), As (0.262), V (0.171), and Cu (0.166). For OP^{GSH}/µg, the best model (R^2 = 0.312) used aqueous Al, As, Ba, Mn, Pb, and V concentrations as predictors; the largest standardized beta coefficients observed were for As (0.435), V (0.312), and Ba (0.175).

EXAMINING THE IMPACT OF THE INTRODUCTION OF THE CCS

TEOM filters were obtained from the filter archives for the six original sites (Bloomsbury—Russell Square, Westminster—Marylebone Road, Camden—Swiss Cottage, Haringey—Town Hall, K & C—North Kensington, and Greenwich—Eltham), encompassing several time periods before the introduction of the CCS, on the February 17, 2003 (see Table 2 for dates of filter collection). The Camden—Shaftesbury Avenue site had initially been identified as a good roadside site within the zone, but it turned out that no filter archive from the site had been maintained. Similarly, Brent—Kingsbury had initially been identified as a good urban background site outside the zone, but no filter archive had been maintained for the dates before introduction of the scheme. Additional details about the sites that were selected are given in Table 3, including site category, location, filter archive collection period, numbers of TEOM filters available 3 years before and after the introduction of the CCS, and average sampling interval. These details highlight some of the key limitations of this data set for assessing the impact of the CCS: filters from only one non-roadside site within the zone were available; there were significant gaps in the time periods for which filters were available at each site before the start of the study; and the time periods over which the filters had been collected were not always concurrent across sites.

Initially, mean PM_{10} concentrations (Figure 7) and oxidative potentials (Figure 8) were examined for the 3 years before and after the introduction of the scheme. This simple descriptive analysis revealed no evidence of change in any measure of oxidative potential at Bloomsbury—Russell Square, the sole within-zone site. In contrast, significant increases in OP^{AA}/µg and OP^{AA}/m^3 were observed at both Westminster—Marylebone Road, the roadside site located on the boundary of the zone, and Camden—Swiss Cottage, the nearby roadside site. However, increases in OP^{GSH} were not observed at these sites, though a statistically significant increase in OP^{GSH}/µg was observed at Haringey—Town Hall, another roadside site located outside the zone, in the 3 years after the introduction of the scheme.

To examine whether these increases in oxidative potential could be attributed to the introduction of the CCS or reflected longer-term trends over the 6-year study period, time-series plots were produced for each of the six original

Table 3. Details of the PM_{10} Filters Collected from the Six Original Sites Used in the Study[a]

Site	Code	Classification	Site Location	Filter Archive Collection Period (Start Date–End Date)	Before CCS	After CCS	Average Sampling Interval (weeks)
Bloomsbury—Russell Square	BL0	Urban background	Within the CCZ	3/21/2001–3/16/2006	30 (71.0%)	41 (91.7%)	3.1 ± 1.2
Westminster—Marylebone Road	MY1	Roadside	CCZ boundary	11/15/2000–3/29/2006	70 (44.7%)	142 (95.1%)	1.1 ± 0.3
Camden—Swiss Cottage	CD1	Roadside	Outside the CCZ	12/14/1999–3/9/2006	37 (44.7%)	34 (46.5%)	2.0 ± 0.8
Haringey—Town Hall	HG1	Roadside	Outside the CCZ	12/14/1999–3/6/2006	61 (76.2%)	27 (63.8%)	2.7 ± 1.3
K & C—North Kensington	KC1	Urban background	Outside the CCZ	1/9/2002–3/13/2006	9 (55.2%)	22 (52.5%)	3.7 ± 1.9
Greenwich—Eltham	GR4	Urban background	Outside the CCZ	1/31/2000–3/17/2006	44 (91.0%)	21 (64.6%)	3.8 ± 1.8

[a] Number (and percentage) of archived TEOM PM_{10} filters collected 3 years before and after introduction of the CCS.

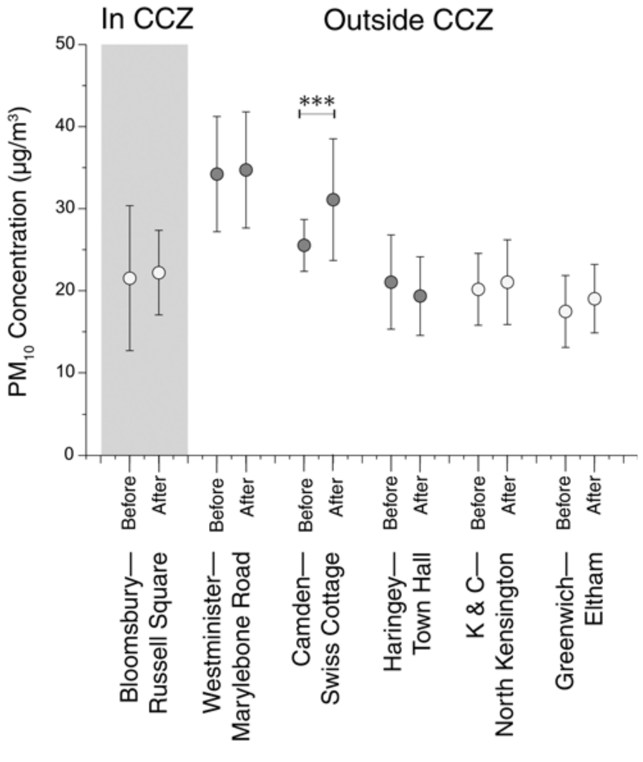

Figure 7. Average ambient PM_{10} concentrations at sites for the 3 years before and after the CCS introduction. Data are means ± 1 SD. The numbers of filters collected from each site are shown in Table 2. The only site in the study that was located fully within the CCZ, Bloomsbury—Russell Square, is shown in the shaded area. Empty circles represent data from urban background sites; filled circles, roadside sites. Comparisons of concentrations before and after the CCS introduction were performed using an unpaired *t* test. $^{***}P < 0.001$.

sites (Figures C.8–C.13). The most complete time series (plotted from data from 212 filters) was derived from the Westminster—Marylebone Road roadside site (Figure C.8), which showed clear upward trends in $OP^{AA}/\mu g$ and OP^{AA}/m^3 over the study period. There were other temporal patterns in the Westminster—Marylebone Road data, but none were clearly interpretable as a change after the introduction of the CCS.

Although no change in the oxidative potential of PM was seen within the zone at the Bloomsbury—Russell Square site (Figure C.9), nominally significant decreases in aqueous Cu, Mn, Ni, and Zn concentrations were observed (Table 4). The decreased concentration of these metals at this site appeared to contrast with general increases in the concentrations of certain metals observed at sites outside the zone. Cu, Ni, and Zn concentrations increased at all but one of the six original sites in the 3 years after the introduction of the CCS (Table 4). Although increases in these metals at K & C—North Kensington, an urban background site, were not significant, they appeared to mirror upward trends over time at most other sites. Mn concentrations appeared to decrease over time at each of the sites.

Spearman rank correlations of PM metal concentrations with $OP^{AA}/\mu g$ and $OP^{GSH}/\mu g$ at each of the original sites are shown in Table C.3. Aqueous Cu, Fe, Ni, and V concentrations were positively associated with $OP^{AA}/\mu g$ in most sites. The relationship between these metals and $OP^{GSH}/\mu g$ was less clear, however; only As was consistently associated with this metric at all of the original sites. Many of the catalytic redox-active metals (Fe, Cu, Ni, and V) had inverse relationships with $OP^{GSH}/\mu g$.

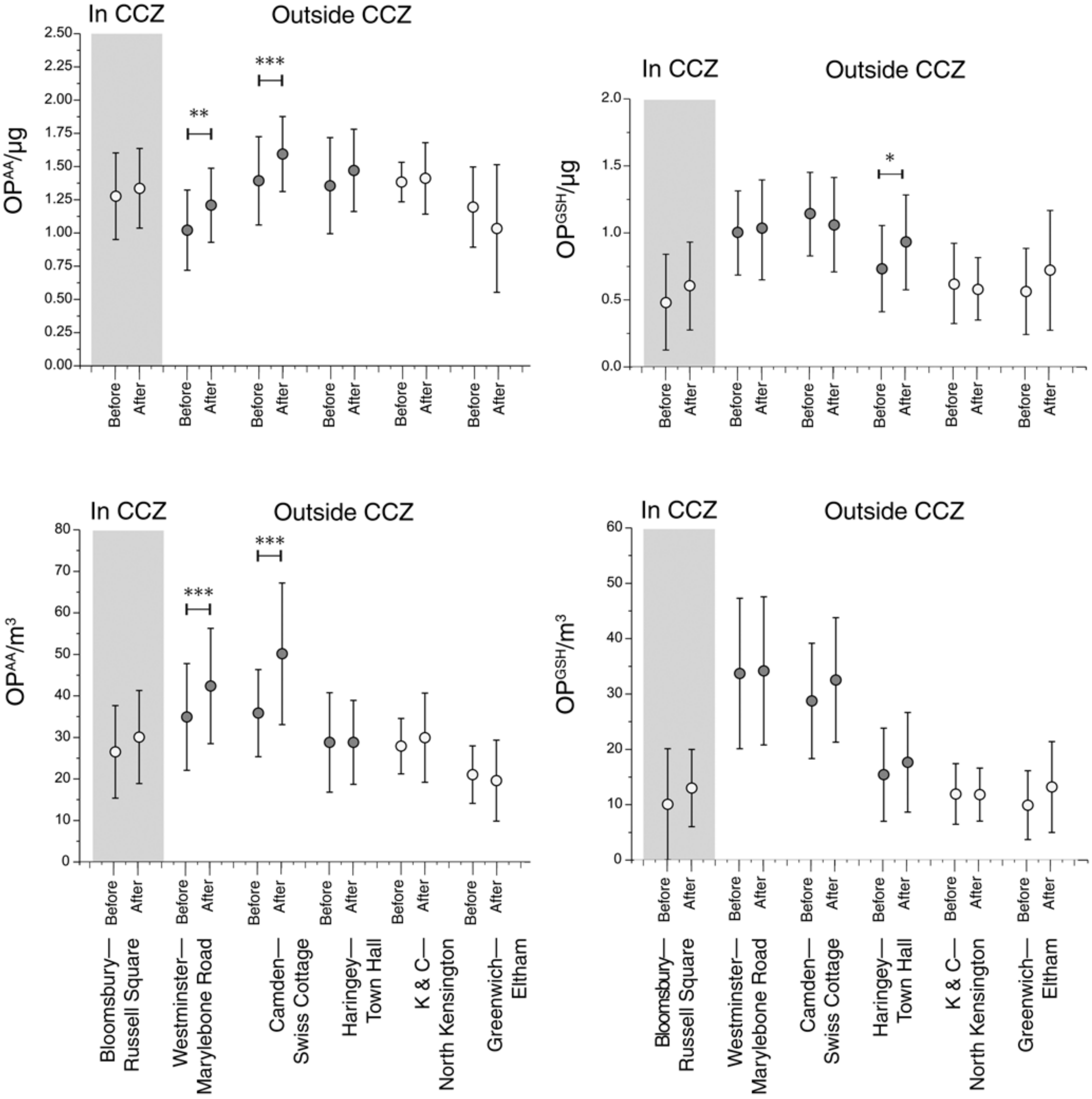

Figure 8. Oxidative potential of PM$_{10}$ from filters collected at sites for the 3 years before and after the CCS introduction. Oxidative potential is expressed per μg of extracted PM$_{10}$ and per m^3 of sampled air. See Figure 7 for details. $^*P < 0.05$, $^{**}P < 0.01$, $^{***}P < 0.001$.

Table 4. Comparison of Aqueous Concentrations of Ten Metals in PM_{10} (ng metal/mg PM_{10}) Collected from the Six Original Sites Before and After the Introduction of the CCS[a]

Site / Filter Collection Period (*n*)	Al	As	Ba	Cu	Fe
Bloomsbury—Russell Square					
Before CCS (29)	196.4 (60.6to252.1)	71.3 (47.1 to 134.3)	62.8 (34.4 to 79.7)	184.3 (138.2 to 212.1)	323.1 (234.9 to 460.4)
After CCS (42)	180.2 (84.2 to 271.5)	82.2 (65.7 to 120.7)	45.8 (30.2 to 94.1)	92.7 (68.4 to 149.3)	295.9 (168.0 to 379.5)
	NS	NS	NS	***	NS
Westminster—Marylebone Road					
Before CCS (70)	156.0 (112.7 to 201.2)	64.3 (45.4 to 99.3)	115.5 (68.5 to 171.4)	108.4 (75.5 to 147.3)	128.4 (83.2 to 241.1)
After CCS (149)	160.3 (84.1 to 227.7)	71.8 (47.8 to 98.3)	168.0 (78.5 to 226.1)	154.2 (102.6 to 299.3)	121.1 (88.2 to 176.6)
	NS	NS	**	***	NS
Camden—Swiss Cottage					
Before CCS (37)	201.7 (160.8 to 396.2)	72.8 (55.5 to 96.1)	129.0 (105.5 to 195.4)	100.0 (70.6 to 134.9)	132.5 (83.7 to 206.4)
After CCS (34)	140.0 (52.1 to 198.0)	87.1 (56.7 to 106.3)	106.5 (54.6 to 177.3)	170.9 (135.1 to 346.2)	210.6 (194.0 to 368.8)
	***	NS	*	***	***
Haringey—Town Hall					
Before CCS (61)	220.0 (162.8 to 361.1)	76.6 (55.9 to 109.5)	75.4 (52.4 to 91.1)	75.9 (54.6 to 100.1)	126.0 (68.2 to 208.1)
After CCS (24)	189.4 (169.0 to 267.8)	114.4 (71.7 to 151.5)	77.2 (40.9 to 142.4)	142.3 (88.4 to 195.1)	169.9 (108.6 to 303.8)
	NS	**	NS	***	NS
K & C—North Kensington					
Before CCS (9)	262.8 (186.9 to 467.6)	73.9 (36.5 to 195.7)	109.7 (57.3 to 147.4)	92.5 (53.7 to 138.6)	214.5 (95.3 to 356.8)
After CCS (22)	157.2 (65.8 to 328.2)	67.3 (49.4 to 101.5)	52.0 (34.4 to 95.8)	100.2 (76.2 to 159.2)	244.5 (106.6 to 430.3)
	NS	NS	NS	NS	NS
Greenwich—Eltham					
Before CCS (44)	219.7 (172.6 to 265.3)	103.0 (68.1 to 129.2)	46.9 (28.9 to 75.3)	60.4 (48.8 to 74.3)	147.1 (85.5 to 209.4)
After CCS (21)	280.9 (190.2 to 426.7)	120.5 (102.9 to 161.2)	53.8 (31.5 to 78.7)	106.4 (83.0 to 133.4)	173.7 (97.1 to 249.7)
	NS	*	NS	***	NS

Table Continues Next Page

[a] Concentrations are expressed as medians (25th to 75th percentiles). Significant differences between metal concentrations in samples collected before and after the introduction of the CCS were determined using the Mann–Whitney U test: NS indicates not significant, $*P < 0.05$, $**\ P < 0.01$, and $***\ P < 0.001$.

WITHIN-CITY SPATIAL VARIATION IN THE OXIDATIVE POTENTIAL OF PM

Because we understood that it would be difficult to retrospectively assess the impact on PM_{10} of the introduction of the CCS, we sought to construct a robust database on the oxidative potential and composition of PM from filters collected before the extension of the CCZ on February 19, 2006. The inclusion of 10 additional sites (i.e., in the Western Extension), which brought the number of sites to 16, also provided the opportunity to perform the first comprehensive study of spatial variability on the oxidative potential of PM in a major city. For this study, PM_{10} from filters collected between December 2004 and March 2006 was extracted and analyzed. Full details of the 16 sites and the number of filters collected from each site are shown in Table 2.

Mean OP^{AA} and OP^{GSH}, expressed per µg PM_{10} or per m^3 ambient air for each of the 16 sites, are ranked in Figure 9. A one-way ANOVA on each of the four data sets revealed statistically significant differences between sites; the differences were observed to be greater for OP^{GSH}. Overall, the oxidative potential of PM collected from the roadside sites was greater than that from the urban background sites (Figure 10), especially when expressed per m^3.

Similar rankings of PM metal content by site are shown in Figure 11 and Figure 12. As was the case for the oxidative potential measurements, a Kruskal–Wallis test (used because the metal data were nonparametric) indicated significant site differences in all the metals examined. Grouping the sites by type of location (i.e., roadside or urban background) revealed that the PM_{10} from the roadside sites had significantly (Mann–Whitney U test) higher concentrations

Table 4 (*Continued*). Comparison of Aqueous Concentrations of Ten Metals in PM_{10} (ng metal/mg PM_{10}) Collected from the Six Original Sites Before and After the Introduction of the CCS[a]

Site / Filter Collection Period (*n*)	Mn	Ni	Pb	V	Zn
Bloomsbury—Russell Square					
Before CCS (29)	102.3 (29.9 to 141.7)	50.4 (34.6 to 63.8)	103.0 (76.7 to 124.0)	108.9 (81.9 to 178.2)	1162.8 (960.2 to 1450.3)
After CCS (42)	26.8 (18.6 to 42.0)	23.2 (14.5 to 32.6)	87.1 (69.3 to 109.6)	162.2 (103.2 to 192.2)	768.8 (558.9 to 938.0)
	***	***	***	NS	***
Westminster—Marylebone Road					
Before CCS (70)	27.9 (18.1 to 40.3)	10.8 (8.5 to 17.5)	49.3 (35.6 to 67.3)	61.4 (32.6 to 87.7)	767.9 (598.8 to 902.6)
After CCS (149)	23.7 (17.6 to 32.0)	17.7 (9.1 to 31.3)	37.6 (23.8 to 52.7)	69.3 (38.7 to 114.1)	895.6 (842.5 to 1204.0)
	*	**	***	*	**
Camden—Swiss Cottage					
Before CCS (37)	87.0 (55.47 to 127.9)	9.8 (7.4 to 17.4)	95.1 (56.8 to 114.9)	80.8 (81.7 to 116.2)	682.9 (551.2 to 877.5)
After CCS (34)	26.5 (20.2 to 47.0)	17.8 (12.0 to 31.2)	46.6 (22.6 to 73.5)	93.7 (40.5 to 159.8)	637.4 (854.4 to 1052.3)
	***	***	***	NS	*
Haringey—Town Hall					
Before CCS (61)	73.6 (41.8 to 155.7)	11.1 (7.3 to 14.7)	101.2 (68.4 to 150.8)	129.3 (88.5 to 186.2)	521.5 (387.4 to 779.3)
After CCS (24)	29.3 (21.9 to 48.5)	21.2 (14.4 to 32.1)	112.9 (66.3 to 177.5)	120.8 (101.0 to 184.0)	827.8 (613.8 to 976.7)
	***	***	NS	NS	***
K & C—North Kensington					
Before CCS (9)	36.9 (34.0 to 91.3)	31.3 (25.4 to 41.8)	100.1 (53.5 to 191.4)	131.2 (92.5 to 195.1)	855.5 (516.7 to 1097.1)
After CCS (22)	25.5 (19.0 to 55.2)	26.4 (21.4 to 31.6)	104.1 (64.9 to 132.6)	117.7 (93.4 to 165.2)	726.5 (602.9 to 795.2)
Greenwich—Eltham					
Before CCS (44)	84.1 (49.8 to 143.6)	11.4 (9.3 to 20.0)	147.3 (103.6 to 211.6)	146.9 (107.5 to 197.5)	458.2 (376.9 to 711.8)
After CCS (21)	32.6 (24.6 to 41.7)	24.6 (20.8 to 33.7)	168.4 (117.6 to 213.1)	206.7 (102.4 to 249.4)	966.6 (596.5 to 1247.4)
	***	**	NS	NS	***

[a] Concentrations are expressed as medians (25th to 75th percentiles). Significant differences between metal concentrations in samples collected before and after the introduction of the CCS were determined using the Mann–Whitney U test: NS indicates not significant, $^{*}P < 0.05$, $^{**}P < 0.01$, and $^{***}P < 0.001$.

of aqueous Ba and Cu; PM_{10} from the urban background sites had higher concentrations of aqueous Al, As, Fe, Pb, and V (Figure 13).

Spearman rank correlations between measures of oxidative potential and concentrations of metals in PM were calculated for three data sets: (1) the data set restricted to the 15-month period (December 2004 to March 2006) stated earlier (Table C.5); (2) the full data set available at each site (Table C.3); and (3) site means (n = 16) estimated from the data set for the 15-month period (Table 5). For both the restricted (Table C.5) and full data analysis (Table C.3), Cu, Mn, V, and Fe had the highest and most consistent positive correlation with OP^{AA}/µg; otherwise, considerable variation was seen across the 16 sites. In contrast, few strong associations were seen consistently for OP^{GSH}/µg across the sites. When OP^{AA}/µg and PM_{10} composition were summarized as mean values across the sites, no significant correlations remained; the highest, though nonsignificant, correlation coefficients were seen for Fe and Cu (Table 5). For mean OP^{GSH}/µg, significant negative correlations were seen with As, Fe, Pb, and V. Only Ba and Cu yielded positive correlations, with only the former being statistically significant.

A similar approach was taken to analyze the copollutant data. Site comparisons were performed on all filters for a given site (Table C.4) and on a subset of filters collected only between December 2004 and March 2006 (Table C.6). The associations between the OP^{AA} and OP^{GSH}/m^3 and copollutant measurements were analyzed as outlined above. Site comparisons were performed on all filters for a given site (Table C.4), as well as on the subset of filters collected only between December 2004 and March 2006 (Table C.6). OP^{GSH}/m^3 was strongly associated with NO_x and

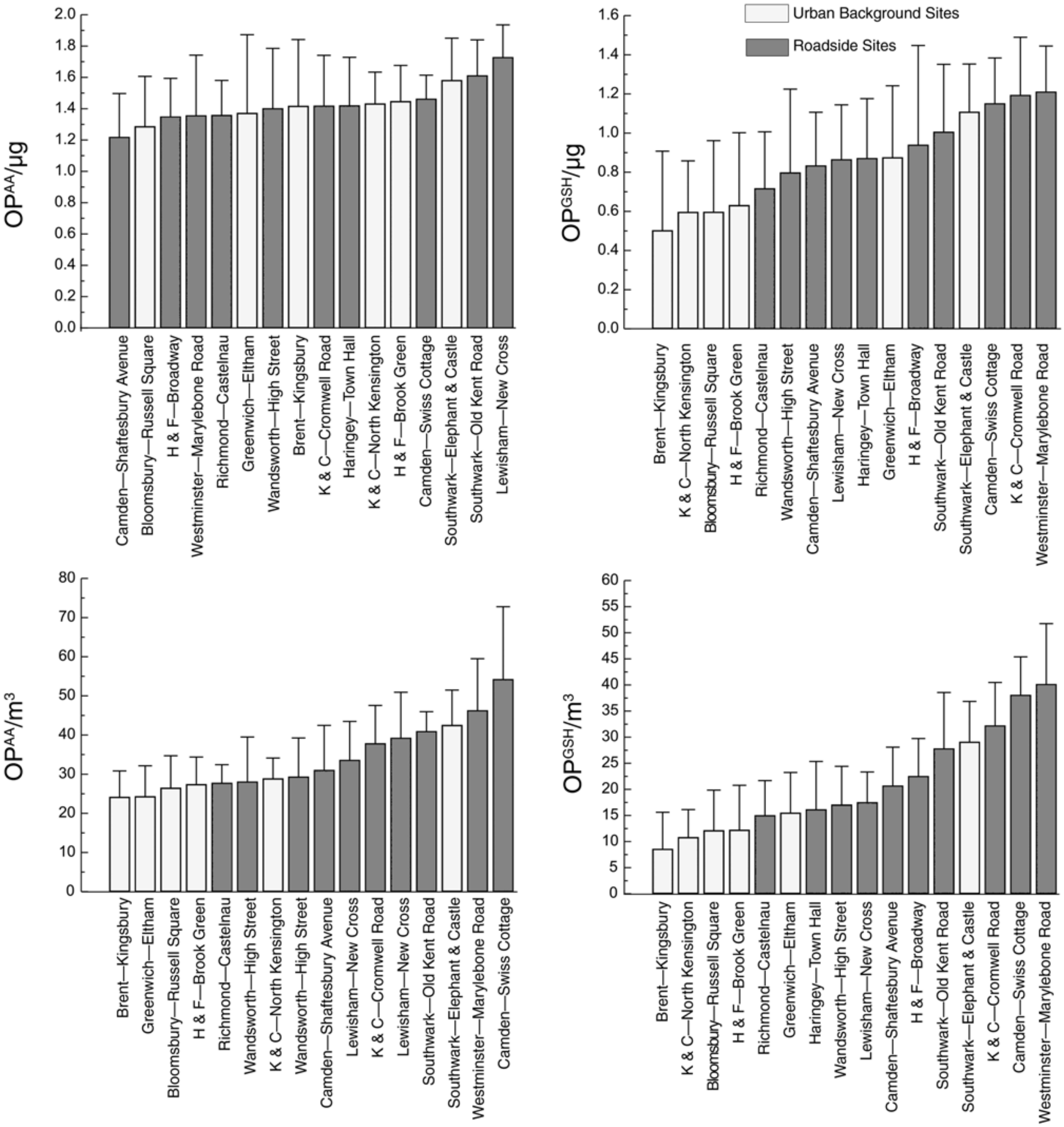

Figure 9. Oxidative potential of PM$_{10}$ measured at 16 roadside or urban background sites in London. Urban background sites and roadside sites are ranked by mean OP^{AA} or OP^{GSH} per µg PM$_{10}$ and per m^3 air. Samples were collected from December 2004 to March 2006. See Table 2 for site details and numbers of filters collected per site.

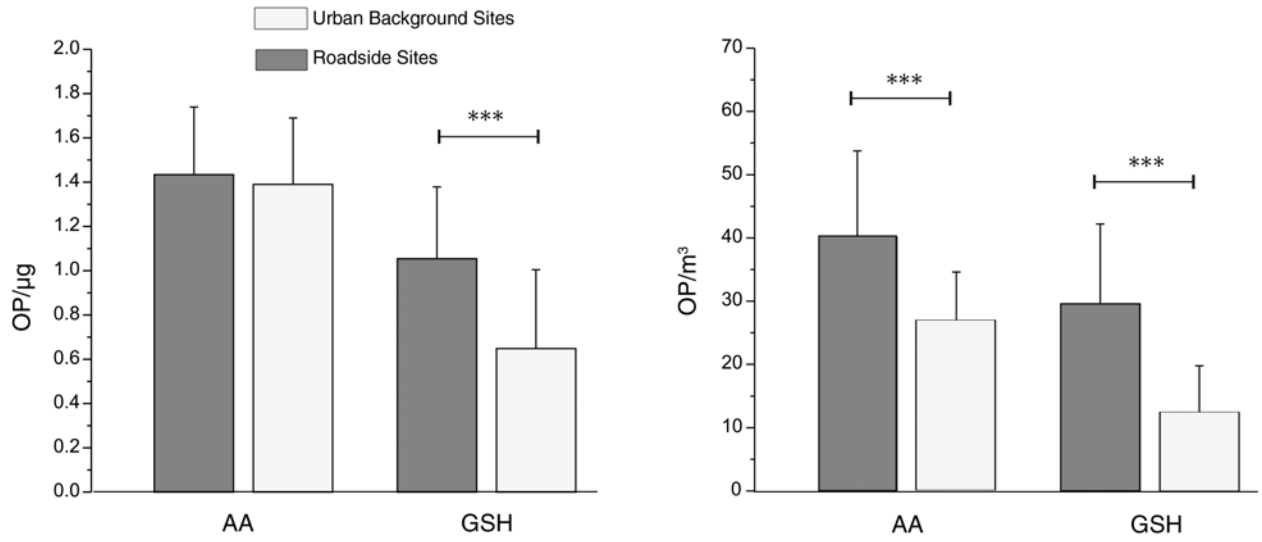

Figure 10. Comparison of oxidative potential (OP^{AA} and OP^{GSH}) per µg PM_{10} and per m^3 air for all urban background and roadside sites. Data are shown are means ± 1 SD of 66 samples from urban background sites and 205 samples from roadside sites. Statistical comparison between the two site categories was performed using an unpaired *t* test. $***P < 0.001$.

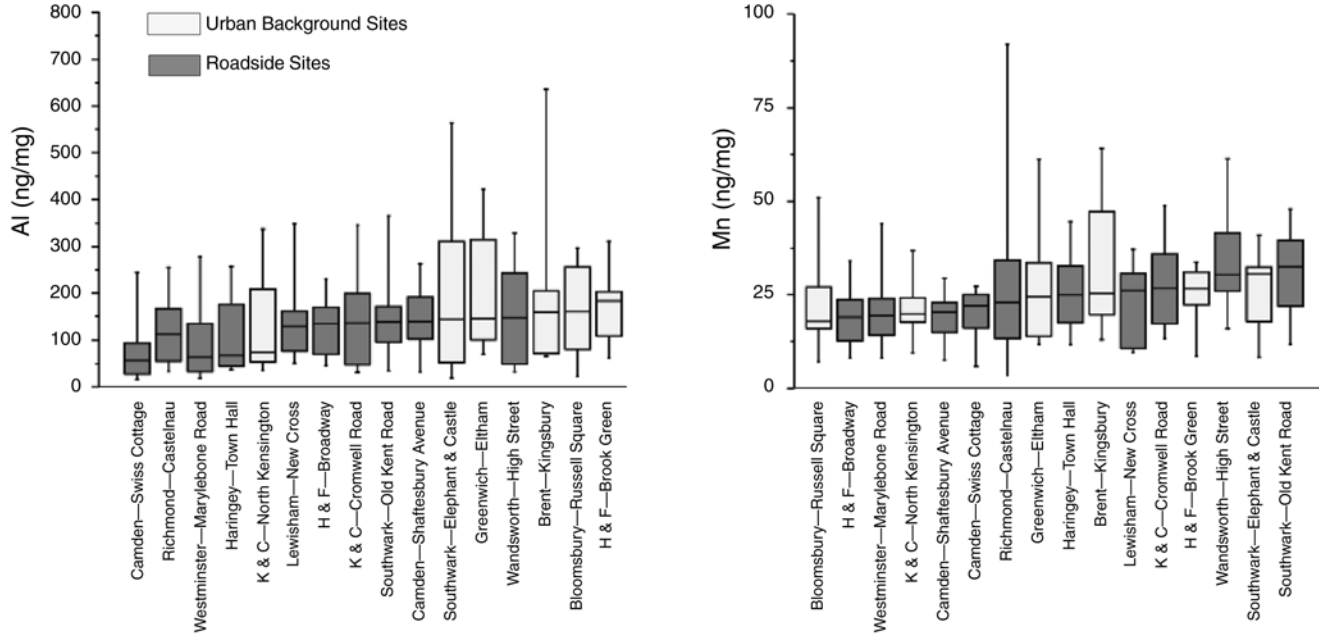

Figure 11. Boxplots of concentrations of six aqueous metals at 16 sites selected to examine contrasts between urban background sites and roadside sites in London. Metals are from samples collected at each of the 16 sites from December 2004 to March 2006. The boxplot displays the median (horizontal line), the interquartile range (box), and the 95th percentiles (whiskers). Boxplots are ranked by median. See Table 2 for site details and numbers of filters collected per site. (*Continues next page*)

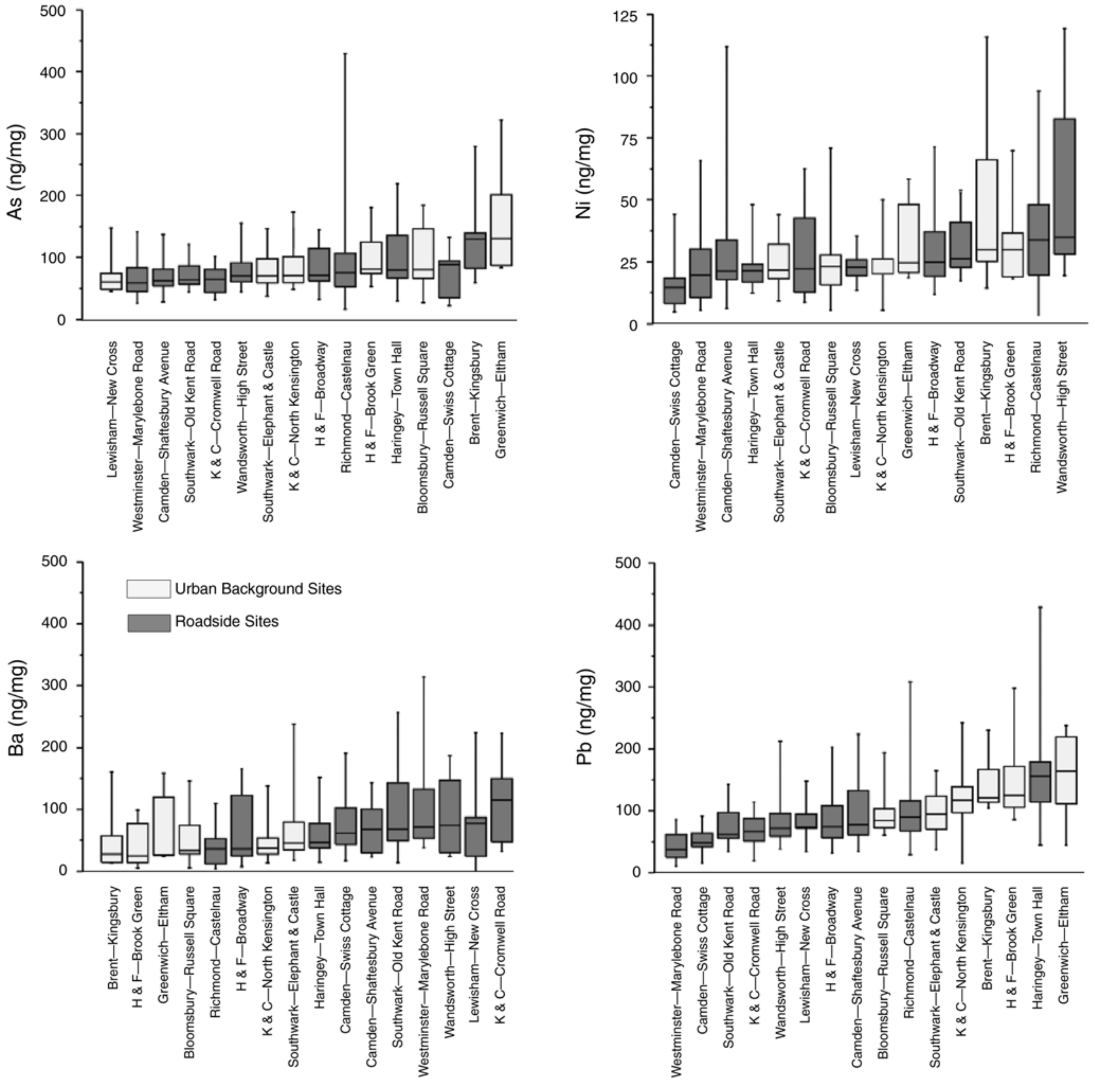

Figure 11 (*Continued*).

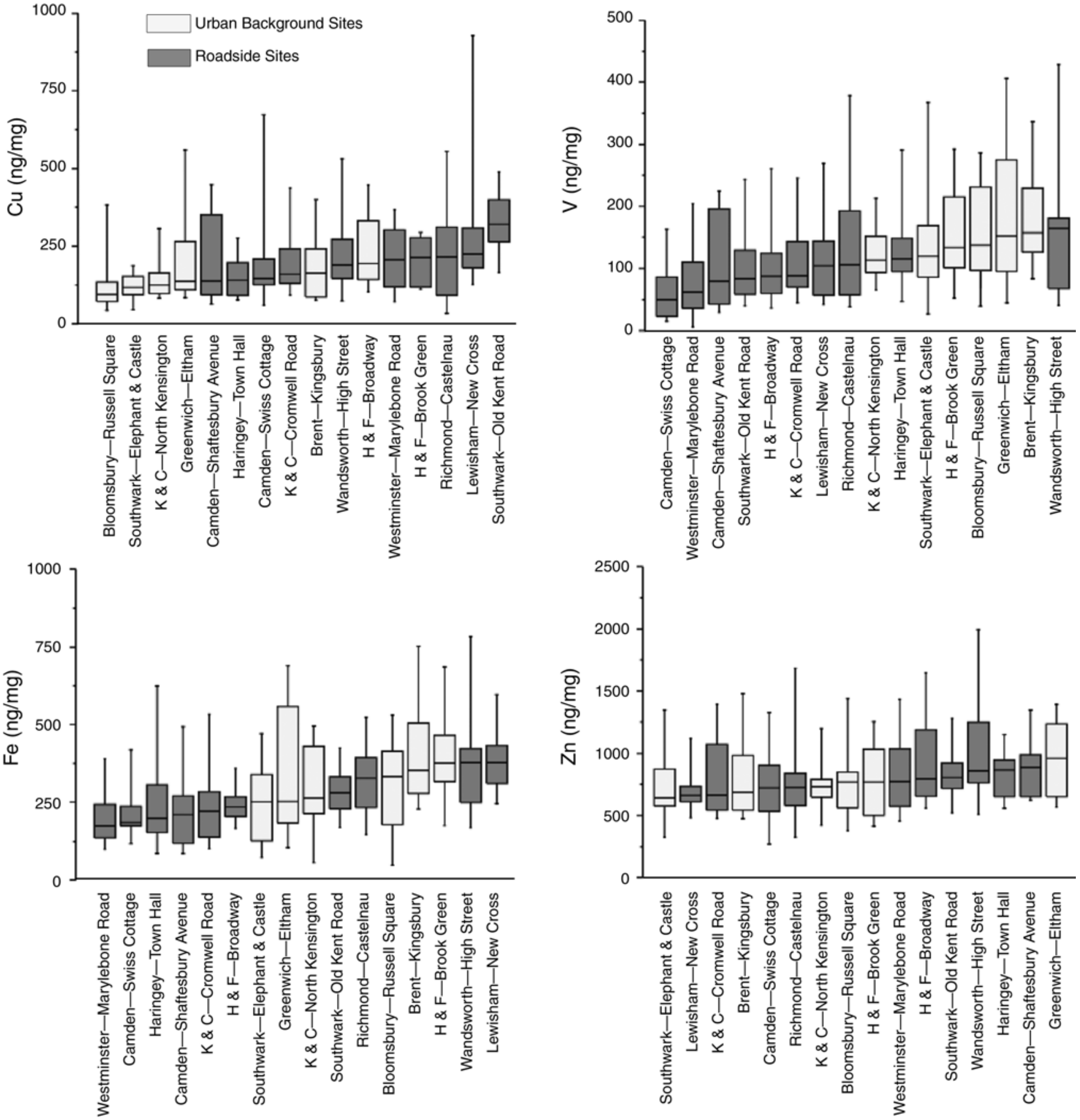

Figure 12. Boxplots of concentrations of four aqueous metals at 16 sites selected to examine differences between urban background sites and roadside sites in London. Metals are from samples collected at each of the 16 sites from December 2004 to March 2006. The boxplot displays the median (horizontal line), the interquartile range (box), and the 95th percentiles (whiskers). Boxplots are ranked by median. See Table 2 for site details and numbers of filters collected per site.

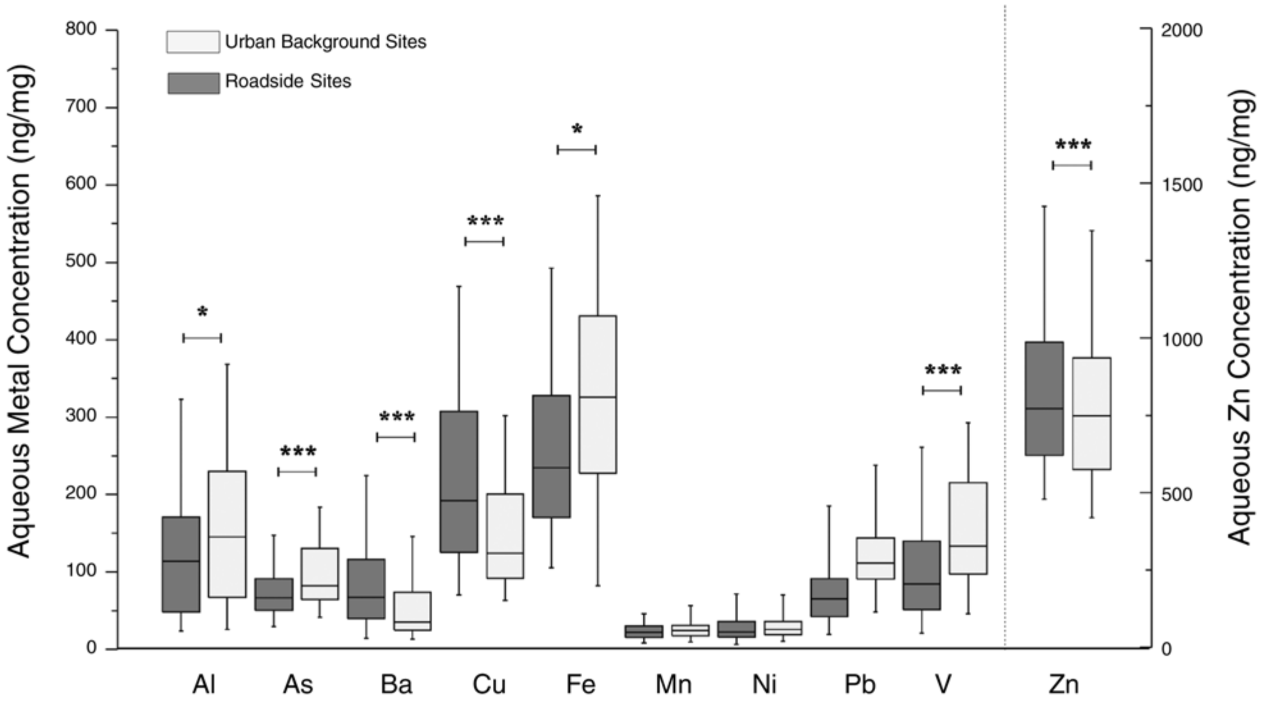

Figure 13. Boxplots of PM_{10} aqueous metal concentrations across all of the urban background and roadside sites investigated in this study. The boxplot displays the median (horizontal line), the interquartile range (box), and the 95th percentiles (whiskers). Statistical comparison between metal concentrations at the two site categories was performed using the Mann–Whitney U test, with statistical differences shown as follows: $^{*}P < 0.05$, $^{***}P < 0.001$ (two-tailed).

Table 5. Associations Between Measures of Oxidative Potential and Mean Concentrations of Aqueous Metals in PM_{10} from All 16 Sites[a]

	OP^{GSH}/µg	Al	As	Ba	Cu	Fe	Mn	Ni	Pb	V	Zn
OP^{AA}/µg	0.096	0.003	−0.072	0.323	0.496	0.353	0.259	−0.103	−0.025	−0.016	−0.172
OP^{GSH}/µg		−0.483	−0.612*	0.666**	0.349	−0.616*	−0.167	−0.246	−0.638**	−0.668**	0.301
Al			0.468	−0.156	−0.065	0.735**	0.671**	0.553*	0.500*	0.765**	0.053
As				−0.776**	−0.094	0.615*	0.329	0.412	0.865**	0.776**	0.065
Ba					0.159	−0.406	0.174	−0.224	−0.638**	−0.479	0.106
Cu						0.294	0.100	0.371	−0.282	−0.088	0.282
Fe							0.512*	0.538*	0.565*	0.812**	−0.071
Mn								0.529*	0.312	0.579*	0.103
Ni									0.282	0.618*	0.600*
Pb										0.756**	0.015
V											0.118

[a] Associations are Spearman rank order correlations. Oxidative potential is derived from measures of depletion of an antioxidant, AA or GSH, indicated by OP^{AA} or OP^{GSH}, respectively. Data on metals were limited to samples collected from December 2004 to March 2006, as described in Table C.5. Concentrations of metals were measured as µg/m³ PM_{10}. $^{*}P < 0.05$ and $^{**}P < 0.01$.

CO, and OP^{AA}/m^3 was more strongly associated with PM_{10} and $PM_{2.5}$.

To further investigate the contributions of Fe and Cu to the oxidative potential of PM_{10}, the chromogenic chelators BPS and BCS were used to determine the concentrations of the surface-mobilizable pools of Fe and Cu, respectively. These analyses were performed on PM_{10} extracts obtained from TEOM filters from each of the 16 sites used in this report, covering the period from December 2004 to April 2006. Fe and Cu concentrations (µM/mg PM_{10}) determined using these chelators are ranked by site in Figure 14. Compared with aqueous Fe concentrations, BPS-mobilizable Fe concentrations were higher in samples from filters collected at roadside sites than at urban background sites. This difference reflected the absence of a quantitative relationship between aqueous and BPS-mobilizable Fe concentrations (Figure C.14). It was also notable that BPS-mobilizable Fe was correlated (Spearman rank order correlation) with both OP^{AA}/µg ($r = 0.23$, $P = 0.01$) and OP^{GSH}/µg ($r = 0.47$, $P < 0.001$) (Figure C.15). BCS-mobilizable Cu was also found in significantly greater concentrations in PM samples from filters collected from roadside sites, which was in agreement with the earlier observation for aqueous Cu (Table 4) and reflecting an underlying association between these two Cu pools (Figure C.14).

Sensitivity Analyses

To test the sensitivity of key results to the clustering of data by site and possible temporal autocorrelation within sites, alternative analyses were conducted. To obtain robust *P* values for associations in the total data set (approximately 730 filters) between ranked metal concentrations and ranked oxidative potential measurements (analogous to the Spearman correlations in Table C.3), regressions were carried out with Huber–White sandwich estimators of standard error (White 1982) based on replication over sites (i.e., STATA command: regress y x, robust cluster

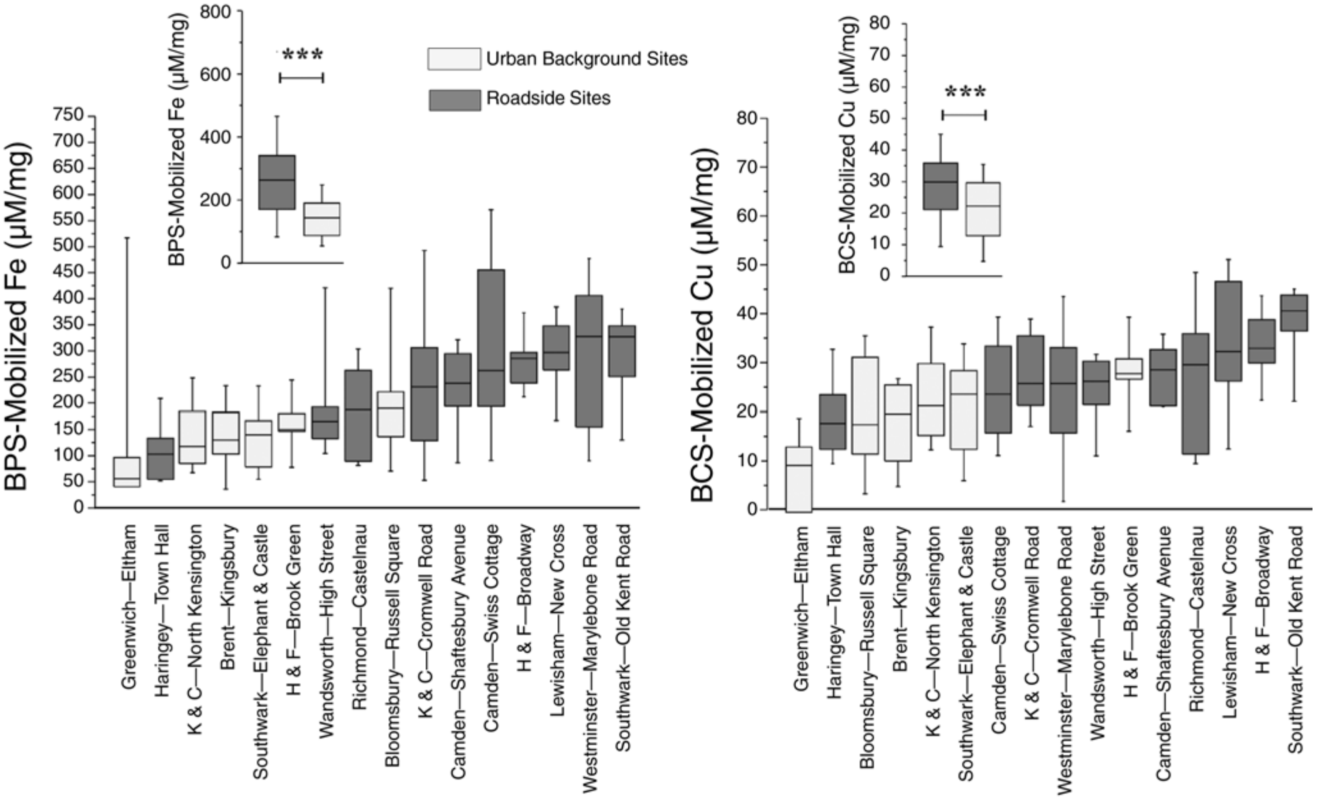

Figure 14. Boxplots of total BPS-mobilizable Fe and BCS-mobilizable Cu concentrations from PM_{10} samples collected from each of the 16 sites in London, ranked by median concentration. Samples were collected from December 2004 to April 2006 from sites selected to show contrasts between urban background and roadside concentrations. The figure inserts show the difference in overall BPS-mobilizable Fe and BCS-mobilizable Cu for all of the urban background and roadside sites. The boxplot displays the median (horizontal line), the interquartile range (box), and the 95th percentiles (whiskers). Statistical comparison between the two site categories was performed using the Mann–Whitney U test, with statistical differences in concentration between the two kinds of sites shown as follows: ***$P < 0.001$ (two-tailed). See Table 2 for site details and numbers of filters collected per site.

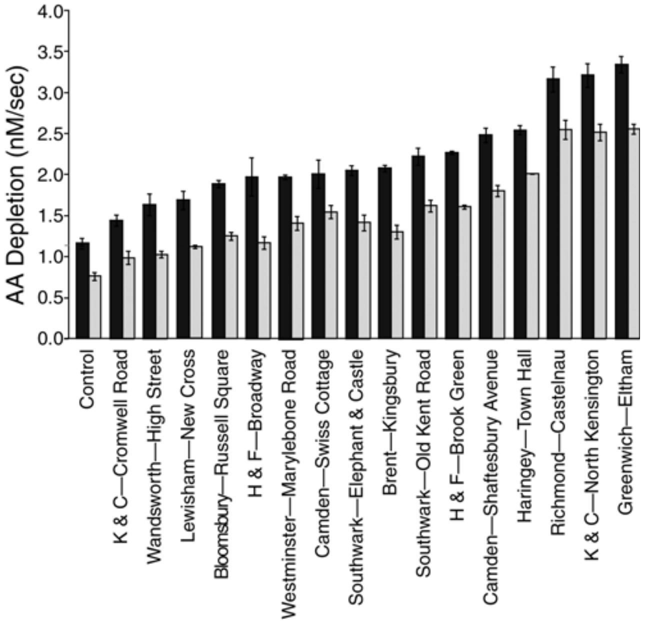

Figure 15. The effect of DTPA on AA depletion rates. Depletion rates of AA were determined using the AA-only model in the presence of 10 µg/mL PM_{10} with (gray bars) and without (black bars) the addition of the metal chelator DTPA (400 µM final concentration). All data are illustrated as the means ± 1 SD of triplicate incubations. Data are ranked by site according to observed rate of AA depletion. See Table 2 for site details. Control indicates effects on particle-free control.

(site)). These analyses confirmed the significance ($P < 0.05$) of overall correlations above 0.1 observed in the earlier analyses between OP^{AA}/µg and metals (i.e., As, Cu, Fe, Mn, Ni, and V) but not those below 0.1 (Al, Ba, Pb, and Zn). Findings for the robust analysis of OP^{GSH}/µg were similar to those of the earlier analysis for most associations (except those for Cu and Zn) that had been identified as significant.

Using the same data as employed for the initial correlation analysis, we also conducted the regressions based on generalized estimating equations to reflect correlation with sites and temporal autocorrelation to order 5 (Zeger et al. 1988). This alternative approach to the previous Huber–White method was somewhat less robust but possibly had more power. These regressions gave P values that fell between the values from the initial (Spearman correlations) and robust analyses; with Al, Ba, and Zn remaining significantly associated with OP^{AA}/µg.

Contributions of Other PM Components to Oxidative Potential

Inhibitor Experiments An additional objective of the study was to investigate the nature of measured PM_{10} oxidative potential through the use of a group of free-radical scavengers and selective metal chelators. Two complementary approaches were used. The first approach used a simple AA-only model, which permitted AA depletion rates to be determined with and without co-incubation with the transition-metal chelator DTPA. The second approach used the synthetic RTLF model with a wider panel of inhibitors.

In the first approach, for each of the 16 sites, a single PM sample was chosen that had an OP^{AA}/µg as close to that of the site mean as possible for the period from December 2004 to April 2006. The AA depletion rates of these samples are shown in Figure 15, ranked by site in comparison with a particle-free control. Given the high concentration of DTPA used, the residual rate after the co-incubation was attributed to nonmetal pro-oxidants (Ayres et al. 2008). On this basis, approximately half of the samples tested had measurable nonmetal contributions to their oxidative potential; these contributions predominated in samples from four sites (Haringey—Town Hall, roadside; Richmond—Castelnau, roadside; K & C—North Kensington, urban background; and Greenwich—Eltham, urban background).

In the second approach, samples were selected from PM_{10} filters collected from 7 of the 16 sites to compare OP^{AA}/µg or OP^{GSH}/µg in PM_{10} collected at roadside and at urban background sites. The extract from a single filter taken from each site was examined. Each sample was chosen because its oxidative potential reflects the mean determined for that site (as shown in Figure 9). The seven sites selected were Bloomsbury—Russell Square (urban background) for low OP^{AA}/µg and OP^{GSH}/µg, Richmond—Castelnau (roadside) for low OP^{GSH}/µg, Westminster—Marylebone Road (roadside) for high OP^{AA}/µg, Southwark—Elephant & Castle (urban background) for high OP^{AA}/µg and OP^{GSH}/µg, Camden—Shaftesbury Avenue (roadside) for low OP^{AA}/µg, and Lewisham—New Cross (roadside) for high OP^{AA}/µg.

Figure 16 shows the concentrations of AA and GSH remaining after a 4-hour incubation of the PM samples, with and without a range of metal chelators and free-radical scavengers. Co-incubation with DTPA significantly decreased AA depletion overall, presumably by inhibiting metal-catalyzed oxidation of antioxidant by chelation. Co-incubation with EDTA actually increased AA depletion in all cases, and DES conferred varying degrees of inhibition of oxidation, from approximately 50% for the samples from Bloomsbury—Russell Square (urban background), Westminster—Marylebone Road (roadside), and Camden—Shaftesbury Avenue (roadside) to almost 100% for the sample from Richmond—Castelnau (roadside). No inhibition was observed with the hydroxyl-radical scavenger DMSO. Co-incubation with the antioxidant enzymes SOD and CAT significantly decreased AA depletion in all cases, including complete inhibition of oxidation in the samples

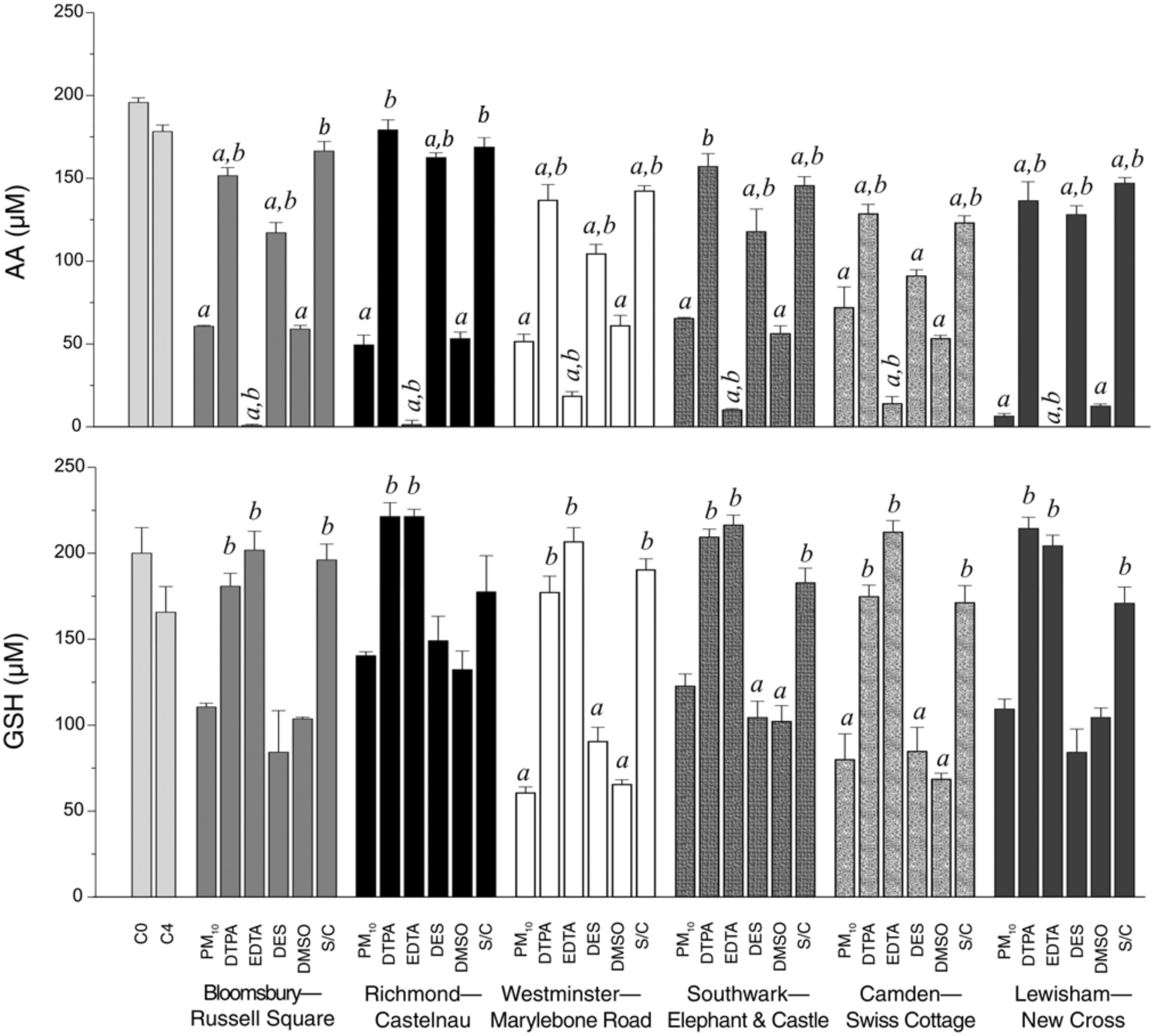

Figure 16. Impact of metal chelation and antioxidant treatment on PM_{10}-induced AA and GSH depletion. Results were obtained after a 4-hour incubation with representative samples from each of the six sites, each sample at a standard concentration of 50 µg/mL. All data represent the means ± 1 SD of triplicate incubations. DTPA = 200 µM diethylenetriamine pentaacetic acid; EDTA = 200 µM ethylenediamine tetraacetic acid; DES = 200 µM desferroxamine mesylate; DMSO = 200 µM dimethylsulfoxide; and S/C = 150 U/mL Cu,Zn-superoxide dismutase and 50 U/mL catalase. Comparison of treatment groups for each PM_{10} sample was performed using a one-way ANOVA with post hoc testing using the Games–Howell test: *a* indicates a significant difference ($P < 0.05$) compared with the particle-free control concentration after the 4-hour incubation (indicated as C4); *b* indicates a significant difference in the treatment groups versus the concentration in the untreated PM_{10} sample at the beginning of the incubation period (indicated as C0). See Table 2 for site details.

from Bloomsbury—Russell Square (urban background) and Richmond—Castelnau (roadside).

Results for OP^{GSH}/µg followed a pattern similar to that of the results for OP^{AA}/µg, with the exception that EDTA was as effective as DTPA in preventing GSH depletion. EDTA was often more effective than DTPA, largely preventing background autooxidation in the samples. DES conferred only minimal inhibition of depletion. Co-incubation with SOD and CAT completely inhibited GSH depletion; DMSO had no inhibitory effect.

Table 6. Source Apportionment of PM_{10} (µg/m^3) in 2005: Comparison of Modeled and Measured Concentrations at All 16 Sites

	Modeled PM_{10}						Measured PM_{10}	
Site	Vehicle Exhaust	Tire Wear	Brake Wear	Primary	Rural	Total	Total	Primary
Bloomsbury—Russell Square	2.3	0.5	0.7	3.5	20.8	24.2	26	5.2
Brent—Kingsbury	0.7	0.2	0.3	1.2	20.2	21.4	21	0.8
Camden—Swiss Cottage	6.9	1.9	2.8	11.6	21.1	32.8	37	15.9
Camden—Shaftesbury Avenue	9.1	1.2	2	12.3	20.8	33.1	34	13.2
Greenwich—Eltham	1.1	0.3	0.5	1.9	20.4	22.2	23	2.6
H & F—Broadway	7.7	2.1	3.1	12.9	20.6	33.5	36	15.4
H & F—Brook Green	1.6	0.5	0.6	2.7	20.6	23.3	24	3.4
Haringey—Town Hall	3	0.9	1.3	5.2	20.5	25.7	25	4.5
K & C—North Kensington	1.4	0.4	0.6	2.4	20.8	23.1	24	3.2
K & C—Cromwell Road	9	2.5	3.6	15.1	20.7	35.8	36	15.3
Lewisham—New Cross	7.3	1.6	2.6	11.5	20.6	32.1	30	9.4
Westminster—Marylebone Road	19	3.7	5.5	28.2	20.6	48.7	43	22.4
Richmond—Castelnau	2.7	0.8	1.2	4.7	20.5	25.2	26	5.5
Southwark—Elephant & Castle	2.8	0.7	1	4.5	20.7	25.2	26	5.3
Southwark—Old Kent Road	6.2	1.7	2.6	10.5	20.6	31.1	32	11.4
Wandsworth—High Street	5.9	1.2	1.8	8.9	20.6	29.5	27	6.4

MODELING OF MOTOR VEHICLE CONTRIBUTIONS TO PRIMARY PM_{10}

Modeling was undertaken to estimate the motor vehicle contributions to ambient PM_{10} in London. Primary PM_{10}, meaning the PM_{10} emitted as part of motor vehicle exhaust and tire and brake wear, was the focus of this effort, because of the associations previously noted between the oxidative potential of PM_{10} and the three metallic elements that are components of tire and brake wear (Cu, Ba, and Zn).

Each PM component was modeled separately from total PM_{10}, and individual concentration surfaces were mapped for London for 2005. From these concentration surfaces, the contributions from each source to total modeled primary PM_{10} were estimated at each of the 16 sites of the study (Table 2) and expressed as gravimetric equivalent PM_{10} (µg/m^3). The predicted PM_{10} concentrations at each of the sites and from each source are shown in Table 6 and compared with measured concentrations. Measured primary PM_{10} was calculated as the measured total PM_{10} at each site minus the modeled rural contribution to PM_{10} (Fuller and Green 2006). Modeled primary PM_{10} and the modeled contribution from vehicle exhaust, tire wear, and brake wear were found to vary markedly across the 16 sites (Figure 17). Using data for

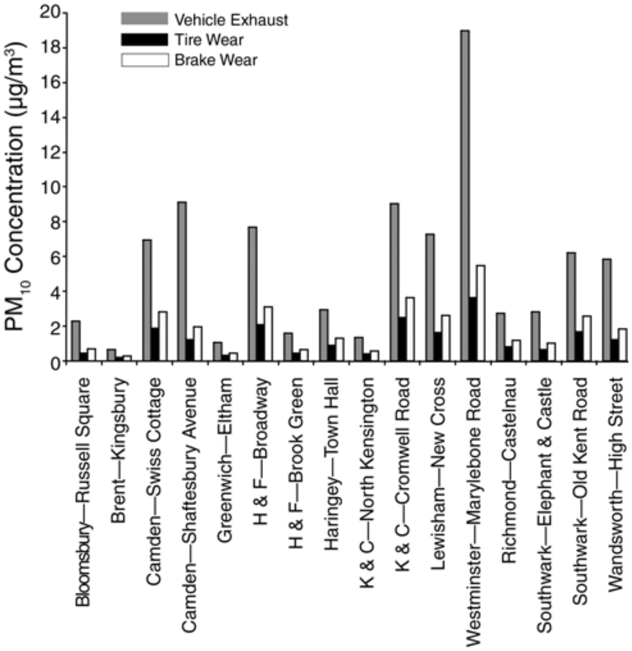

Figure 17. The modeled contributions of vehicle exhaust, tire wear, and brake wear to PM_{10} at 16 sites in London in 2005.

all 16 sites, correlations were assessed between primary PM$_{10}$, its components (vehicle exhaust, tire wear, and brake wear), modeled rural PM$_{10}$, and total PM$_{10}$ (i.e., primary plus rural PM$_{10}$) and oxidative potential (see Table 6). The analysis showed significant correlations between each of the three vehicular sources of primary PM$_{10}$ and primary PM$_{10}$, total PM$_{10}$, but not with rural PM$_{10}$. We note however that there was little difference in concentrations of rural PM$_{10}$ between sites (Figure 18). The high degree of correlation between each of these variables (vehicle exhaust, tire wear, brake wear, and primary PM$_{10}$) prevented attribution of actual oxidative potential measurements to any single variable.

When ambient PM concentrations are expressed as μg/m^3, some degree of correlation might be expected with oxidative potential expressed per m^3. The analysis was therefore repeated after expressing the modeled primary and rural PM$_{10}$ contributions as a percentage of the total modeled PM$_{10}$ (Table 7). Again, strong associations were found between oxidative potential and the percentages of total modeled PM$_{10}$, but the high degree of correlation between each of the sources again limited the interpretation of these results.

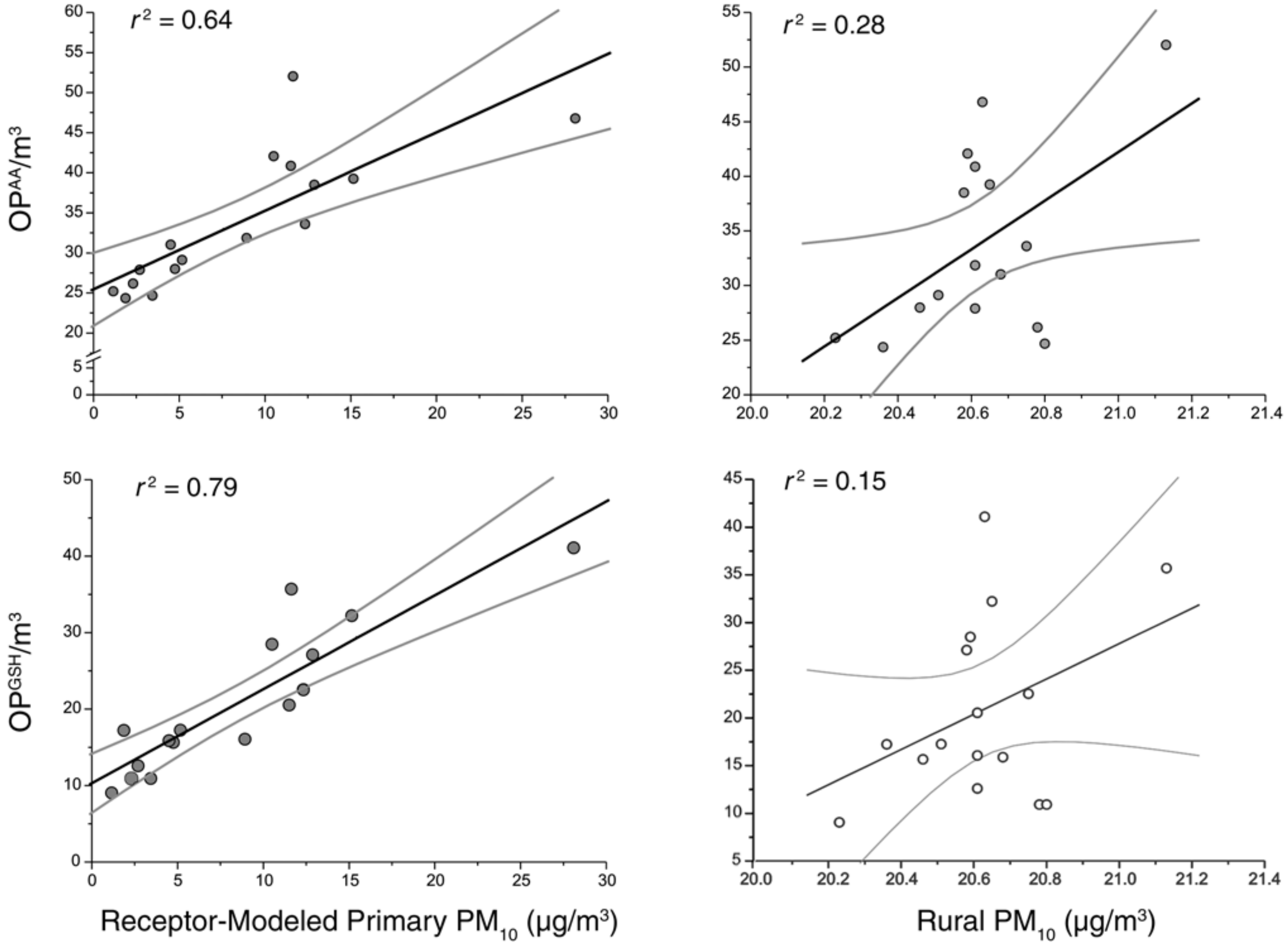

Figure 18. The associations between oxidative potential of PM$_{10}$ samples collected in 2005 and modeled concentrations of receptor-modeled primary PM$_{10}$ and rural PM$_{10}$ (equivalent to measured PM$_{10}$ minus the modeled primary PM$_{10}$) for the same year. Oxidative potentials are expressed as OP^{AA} and OP^{GSH} per m^3 of air. Linear regressions with 95% confidence intervals have been fitted to each data set; resultant r^2 values are shown in each panel. Note differences in scales.

Table 7. Associations Between Measures of Oxidative Potential and Modeled Concentrations of PM_{10} from Various Sources[a]

	OP^{GSH}/m^3	Vehicle Exhaust PM_{10}	Tire Wear PM_{10}	Brake Wear PM_{10}	Primary PM_{10}[b]	Rural PM_{10}	Total PM_{10}
Associations with Modeled Concentrations of Primary and Rural PM_{10}							
OP^{AA}/m^3	0.868**	0.862**	0.915**	0.914**	0.874**	0.295	0.874**
OP^{GSH}/m^3		0.862**	0.909**	0.905**	0.885**	0.177	0.885**
Vehicle exhaust PM_{10}			0.944**	0.948**	0.985**	0.324	0.985**
Tire wear PM_{10}				0.999**	0.979**	0.26	0.979**
Brake wear PM_{10}					0.982**	0.263	0.982**
Primary PM_{10}						0.292	1.000**
Rural PM_{10}							0.292
Associations with Modeled Concentrations of Primary and Rural PM_{10} Expressed as Percentages of Modeled Total PM_{10}							
OP^{AA}/m^3		0.862**	0.921**	0.912**	0.865**	−0.865**	
OP^{GSH}/m^3		0.862**	0.900**	0.897**	0.871**	−0.871**	
Vehicle exhaust PM_{10}			0.924**	0.926**	0.988**	−0.988**	
Tire wear PM_{10}				0.997**	0.959**	−0.959**	
Brake wear PM_{10}					0.962**	−0.962**	
Primary PM_{10}						−1.000**	

[a] Associations are Spearman rank order correlations. Oxidative potential is derived from measures of depletion of an antioxidant, AA or GSH, indicated by OP^{AA} or OP^{GSH}, respectively. PM_{10} concentrations for all 16 sites were modeled for the year 2005. **$P < 0.01$.

[b] Primary PM_{10} concentration is defined as the sum of the concentrations of PM_{10} from vehicle exhaust, tire wear, and brake wear.

DISCUSSION

ASSESSMENT OF THE OXIDATIVE POTENTIAL AND METAL CONTENT OF PM_{10}

We examined the capacity of PM_{10} collected from designated sites in London to deplete antioxidants from synthetic RTLF, thereby providing an estimate of its oxidative potential. There is a growing consensus among toxicologists that the capacity of inhaled PM to cause oxidative stress at the air–lung interface by inducing inflammation through redox-sensitive cell signaling pathways (Pourazar et al. 2005) might underlie many of the acute and chronic health effects observed in epidemiologic studies (Borm et al. 2007). Induction of redox-sensitive cell signaling pathways has been linked to PM transition metals, quinone, and PAH content (Bonvallot et al. 2001; Li et al. 2003; Borm et al. 2007). A simple measure of oxidative potential that effectively integrates differences in PM composition and size distribution could therefore be useful as a PM metric relevant to human health. The synthetic RTLF model was used both because of its relevance to in vivo conditions by modeling reactions that are likely to occur when PM is inhaled and because it is well validated assay that has been used previously to assess the oxidative potential of a variety of PM models (Zielinski et al. 1999; Mudway et al. 2004), ambient PM (Künzli et al. 2006), and the oxidant gases O_3 (Mudway and Kelly 1998) and NO_2 (Kelly and Tetley 1997).

Before discussing the findings of the study in the context of the impact of the introduction of the CCS or in terms of spatial variations in the oxidative potential of PM_{10}, several observations are warranted about our data on oxidative potential examined at the level of individual samples. Considerable variation between filters was observed in the capacity of extracted PM_{10} to deplete AA in the RTLF assay. In particular, a substantial proportion of the samples had oxidative potential equal to or greater than that of our positive control (ROFA) when compared at the same concentration. This result was even more marked in the case of the depletion of GSH, in which no depletion was observed for the positive control. These two results clearly demonstrate the potency of London's ambient PM_{10}. The lack of GSH depletion in the positive control suggests that the principal soluble metals associated with ROFA — V, Zn, Fe, and Ni — do not catalyze GSH depletion in the synthetic RTLF model and that, instead, Cu might largely drive the depletion.

The capacity of soluble metal salts and quinone compounds to oxidatively deplete antioxidants in the synthetic RTLF model has been investigated previously (Ayres et al. 2008). We showed that Cu salts promote the oxidative loss of both AA and GSH from synthetic RTLF but Fe salts predominantly oxidize AA. Ni and V catalyze limited AA oxidation in this model, and Zn salts do not catalyze either AA or GSH oxidation (Ayres et al. 2008). The capacity of quinone compounds to catalyze the depletion of AA is well established (Roginsky et al. 1999, 2000); however, the literature shows that quinones will not catalyze the depletion of monothiols, such as GSH (Kumagai et al. 2002). Hence, measurements of oxidative potential derived from the capacity of PM to deplete AA or GSH from synthetic RTLF reflect slightly different catalysts and mechanisms. These differences help to explain why our two metrics are only weakly associated.

Using our antioxidant depletion data, expressions were derived for the oxidative potential of ambient PM_{10} per µg of PM_{10} mass, assuming that the dose–effect relationship for all samples was the same. This assumption is clearly an oversimplification but does permit an expression to be derived for the oxidative potential of ambient PM_{10} expressed per m^3, which is a meaningful indicator of the oxidative potential of ambient PM_{10} at a given location and for the sampling period.

UA was not depleted from the synthetic RTLF by any of the ambient PM or model experimental particles examined, consistent with our earlier findings (Mudway et al. 2004, 2005a,b; Künzli et al. 2006). This suggested that UA was neither playing a role in the reduction of PM-associated metals nor scavenging reactive-oxygen species from metal-catalyzed reactions. Hence, although UA is highly effective in conferring protection against O_3 and NO_2, it does not appear to play an important role in protecting against inhaled PM. Because UA reacts with hydroxyl radicals at a rate that is broadly similar to that of both AA and GSH (7.2 nmol/sec, 1.6 nmol/sec, and 9.0 nmol/sec, respectively), its lack of reactivity implies that hydroxyl radicals were not involved in the observed depletion of AA and GSH. This conclusion was further supported by the lack of protection observed against PM-induced AA and GSH oxidation when co-incubated with the hydroxyl-radical scavenger DMSO (Slivka and Cohen 1988).

IMPACT OF THE CCS ON THE OXIDATIVE POTENTIAL OF AMBIENT PM_{10} IN LONDON

The principal objective of this study was to test the hypothesis that the introduction of the CCS in London in February 2003 and the associated changes in density and type of traffic affected the oxidative potential of the city's ambient PM_{10}. This hypothesis assumed that traffic-related PM components (i.e., motor vehicle exhaust, tire wear, brake wear, and resuspended road dust) contributes significantly to the oxidative potential of PM_{10} in urban environments. To address this hypothesis, archived TEOM PM_{10} filters were obtained from six air-pollution monitoring sites throughout London. The sites were located within, bordering, or outside the CCZ and were in operation for the 3 years before the introduction of the scheme. Plans were made to collect filters from these sites for 3 years after the introduction of the CCS in order to permit comparisons of PM oxidative potential and component concentrations before and after the scheme's introduction. Initially, we had hoped to obtain TEOM PM_{10} filters from both an urban background site and a roadside site within the zone; however, no archived filters were available from a roadside site. Our analysis was therefore restricted to one urban background site (Bloomsbury—Russell Square) within the zone. Because the impact of the CCS was expected to be felt most strongly at roadside sites inside the zone, the absence of samples from such sites represents a major weakness of the study.

In addition, as data were gathered and checked, it was noted that in 2002 the ratios of PM_{10} to $PM_{2.5}$ at Bloomsbury—Russell Square were high in comparison with those of previous years. Further investigation identified a step change in the PM_{10} baseline at Bloomsbury—Russell Square in June 2002 that occurred at the same time as the replacement of a TEOM control unit at this site on June 25, 2002. Additional testing revealed a discrepancy in the TEOM calibration factor; however, this discrepancy alone failed to account for the step change in the data. Additional instrument or database information could not be found to explain the step change. As a consequence, no validated PM mass data were available for Bloomsbury—Russell Square from June 25, 2002, to May 21, 2003 (when a new TEOM was installed at the site). Instead, PM_{10} mass on filters collected between these dates was established by weighing. This additional step increased uncertainty in the data collected during this important period.

Given these caveats, no overall change was observed in the oxidative potential of PM_{10} (expressed either per µg PM_{10} or per m^3 ambient air) at the Bloomsbury—Russell Square urban background site during the 6 years of data examined in the study. In contrast, OP^{AA} increased significantly in PM_{10} collected from two roadside sites, one bordering the CCZ (Westminster—Marylebone Road) and the other outside the CCZ (Camden—Swiss Cottage). However, no changes in OP^{GSH} were observed in the PM_{10} from the same two sites. Examination of time-series data from Westminster—Marylebone Road demonstrated a significant upward trend in OP^{AA} over the 6-year period (see Figure C.9). There was some evidence of a leveling off for a 12-month period after the introduction of the CCS, which suggested that the increased OP^{AA} observed in samples from this site could not be attributed simply to the introduction of the scheme, but rather reflected the influence of a longer trend.

Although change in the oxidative potential of PM_{10} was not seen within the zone at Bloomsbury—Russell Square (Figure C.9), nominally significant decreases in aqueous Cu, Mn, Ni, and Zn concentrations were observed (Table 4). The decreased concentrations of these metals at this site appeared to contrast with general increases in the concentrations of certain metals observed at sites outside the zone. Cu, Ni, and Zn concentrations increased at all but one of the six original sites in the 3 years after the introduction of the CCS (Table 4). Although increases in these metals at K & C—North Kensington, an urban background site, were nonsignificant, they appeared to increase upward trends over time at most other sites. Mn concentrations appeared to decrease over time at each of the sites.

The upward trend observed in the oxidative potential of PM_{10} from the Westminster—Marylebone Road site is striking. One possible interpretation of this trend is that it reflects a storage artifact and hence a time-dependent loss of oxidatively active components in the archived filters. For the period before the introduction of the CCS, our study was limited to the use of archived filters; these had been stored for up to 4 years at room temperature. For consistency's sake, filters collected by us during the study were therefore stored under similar non-ideal conditions. We reasoned that, because the filters were from TEOM monitors, which had been heated to 50°C, most volatile components (predominantly ammonium nitrate and volatile organic aerosols) would already have been lost and that the remaining components (particularly metals) would be stable over time. It should be noted that, because filters were extracted and resuspended based on their calculated mass — a calculation that was not final until the data had undergone a rigorous ratification procedure — there was a lag of at least 1 year between collection and analysis for all filters. It was also notable that the relationship between the age of the filter and OP^{AA} was not evident at all of the examined sites. This relationship was evident at Westminster—Marylebone Road, the site that yielded the most comprehensive time series.

Although some effect from the age of the filters cannot be completely excluded from the data set, it is possible that the upward trend in oxidative potential observed at Westminster—Marylebone Road was real and reflected a significant change in PM_{10} composition, particularly at sites such as Westminster—Marylebone Road, which were located at the border of the zone. A study by Fuller and Green (2006) demonstrated increasing concentrations of primary PM_{10} in London from 2000 to 2005, including at Westminster—Marylebone Road. This increase has subsequently been shown to be more widespread and has been proposed as one of the possible explanations for the slowing down in reductions of PM_{10} concentrations across Europe (Harrison et al. 2008). Consistent with a change in PM composition driving the increased OP signal at Westminster—Marylebone Road over time, we observed a moderately positive, but statistically significant increase in aqueous Cu PM_{10} content at this site over the sampling period. We interpreted this as reflecting an increased emission from brake wear, paralleling the previously noted increase in primary PM_{10} at this site.

To examine the contribution of volatile species to the oxidative potential of PM_{10} we took advantage of colocated TEOM and FDMS monitors at two sites in London (Appendix B). The oxidative potential of PM_{10} samples collected on FDMS base (collected at 30°C) and purge (collected at 4°C) filters was compared with that of samples collected on the TEOM filters (collected at 50°C). Little evidence was found to support the contention that volatile species contributed to the oxidative potential of PM_{10}. Thus the measurements of oxidative potential made in the current study do not appear to exclude significant contributions by volatile species.

WITHIN-CITY SPATIAL VARIATION IN THE OXIDATIVE POTENTIAL OF PM_{10}

In addition to examining temporal changes associated with the introduction of the CCS, we also examined spatial variations in the oxidative potential and composition of PM_{10}. This analysis included filters collected between December 2004 and March 2006 from the six original sites and the 10 additional sites associated with the Western Extension of the CCZ. In addition to the considerable variability in oxidative potential over time noted for filters collected at all 16 sites, spatial variability (i.e., site-dependent differences) was apparent amongst sites. OP^{GSH} was higher in samples from filters collected from roadside sites than from urban background sites. This increased oxidative potential appeared to reflect increased concentrations of aqueous Cu and Ba as well as BPS-mobilized Fe in the samples from roadside sites. Notably, the roadside samples did not have higher concentrations of aqueous Fe. As stated earlier, the panel of metals examined in the filters extracts were selected to reflect known traffic sources based on published data (de Miguel et al. 1997; Onianwa 2001;

Weckwerth 2001; Manoli et al. 2002; Harrison et al. 2003; Laschober et al. 2004; Zechmeister et al. 2005).

After investigation of the relationship between aqueous and ligand-mobilized pools of metals (in this case, the ligands were AA, the synthetic RTLF antioxidants, and citrate), all subsequent analyses for metals in the PM samples were determined in aqueous extracts. Although incubation of PM in citrate resulted in increased mobilization of the majority of the metals examined, including Fe, as has been demonstrated previously (Smith et al. 1998; Aust et al. 2002), little difference in metal concentrations was noted between PM incubated in water and in synthetic RTLF. Furthermore, highly significant associations were noted between the metal concentrations in water and those in synthetic RTLF. The capacity of the chromogenic chelators BPS and BCS to bind and mobilize Fe and Cu on particle surfaces was also examined.

Although sources of PM other than vehicle exhaust are widely acknowledged, they have received less attention than vehicle exhaust in the study of air pollution and human health effects. This focus partially reflects the assumption that PM from non-exhaust sources consists largely of coarse fraction of PM ($PM_{2.5–10}$) and hence is not inhaled deeply into airways. Tire wear is thought to be the largest non-exhaust source of total suspended particles (TSP) and PM_{10} (Lükewille et al. 2001). Although there is considerable disagreement in the literature about the contribution of tire wear to ambient PM, conservative estimates suggest emission rates of approximately 100 mg/vehicle km traveled (Councell et al. 2004; Boulter 2006); higher rates are associated with heavy-duty vehicles (Legret and Pagotto 1999). About 90% of the particles emitted can be classified as PM with an aerodynamic diameter of ≤ 1 µm (PM_1) (Fauser 1999). Other studies have shown that 70% of the mass of PM_{10} from tire wear can be classified as $PM_{2.5}$, 10% as PM_1, and 8% as $PM_{0.1}$ (Berdowski et al. 1997). There is also evidence that particle diameter decreases with increased vehicle speed (Dannis 1974).

Zn has been used as a tire-wear tracer, because it has few other vehicle-related sources (Fauser 1999). Al, Cu, Fe, and Ba are also associated with tire wear, but these are present at concentrations orders of magnitude lower than that of Zn. The increase in Zn concentrations in ambient PM_{10} after the introduction of the CCS may therefore be interpreted as reflecting increased vehicle numbers within London, increased vehicle miles traveled in London, changes in tire composition, or — as has been reported — evidence of a heavier vehicle fleet (Carslaw 2006). It was notable, however, that Zn was not quantitatively associated with any measure of oxidative potential, reflecting its stable electron configuration.

Brake wear, namely the wear of brake linings and rotors resulting from frictional heating during forced deceleration, is also considered to be a source of PM_{10}. The amount of PM attributed to brake wear is somewhat less than that attributed to tire wear. In light-duty vehicles, brake wear contributes approximately 10–20 mg/vehicle km traveled (Legret and Pagotto 1999; Garg et al. 2000); in heavy-duty vehicles the contribution doubles (Kennedy et al. 2002). When quantified by mass, 98% of brake-wear dust is PM_{10}, of which 40% is $PM_{2.5}$, 10% is PM_1, and 8% is $PM_{0.1}$ (Berdowski et al. 1996).

The metals present in the highest concentrations in brake-wear dust are Fe, Cu, Zn, and Pb. Cu concentrations vary from 10–20 mg/vehicle km to 50–80 mg/vehicle km for light-duty and heavy-duty vehicles (Boulter 2006). Other metals (e.g., Ba, calcium [Ca], Mn, Ni, antimony [Sb], and Sn) have also been shown to be associated with brake-wear dust (Sternbeck et al. 2002; Boulter 2006).

In the current study, three of these metals (Fe, Cu, and Ba) were found to be associated with both OP^{AA} and OP^{GSH}. Although Fe and Cu are both redox-active metals (Buettner and Jurkiewicz 1996), the Ba association would seem to be more directly related to brake wear because it is present in barite, a common brake-pad filler. Associations between Mn, As, and Cd and oxidative potential were also observed. The concentrations of these metals in road dust have been attributed to brake wear, and quantitative associations have been observed between the amount of these metals in PM dust and vehicle numbers (Kennedy 2003).

The finding in the current study that the association between PM_{10}'s oxidative potential and Fe content was stronger for BPS-mobilized Fe than for aqueous Fe is notable. The biologic relevance of BPS Fe relates to the comparability of its stability constant for Fe (1×10^{22}/M) (Nilsson et al. 2002) to that of the endogenous chelator transferrin ($1 \times 10^{22–28}$/M), the principal Fe-transport protein in RTLF (Aisen and Listowsky 1980; Halliwell and Gutteridge 2007), and in the presence of an excess of citrate (1×10^{16}/M; Halliwell and Gutteridge 2007). Hence, BPS-mobilized Fe provides a measure of the amount of Fe likely to be mobilized from the particle surface in vivo, both in RTLF and in the intracellular environment.

The fact that aqueous Fe concentrations were higher at urban background sites and BPS-mobilized Fe concentrations were higher at roadside sites might reflect differences in the form of Fe from crustal and vehicle-related sources. Fe exists in a number of oxide forms, including hematite (Fe_2O_3) and magnetite (Fe_3O_4), which are thought to be relatively inert (Aust et al. 2002). However, other forms, such as ferric oxyhydroxides, can be more reactive, as is Fe associated with silicates. Fe associated with silicates has been shown to be present in coal fly ash and is rendered bioavailable in the presence of citrate (Veranth et al. 2000). Veranth and colleagues (2000) demonstrated that, when incubated in the presence of desferroxamine, coal fly ash was stripped of the Fe associated with its aluminosilicate-glass fraction. This incubation greatly reduced the amount of Fe mobilized by citrate in a subsequent incubation, implying an almost exclusive localization of bioavailable Fe in the aluminosilicate-glass fraction. Brake pads have also been shown to contain high concentrations of silicon compounds (Hildemann et al. 1991), and one might therefore speculate that the Fe in brake-wear emissions might exist with silicates.

Resuspension of road dust by traffic-generated turbulence also represents a significant source of non-exhaust PM; indeed, numerous studies have suggested that resuspended road dust constitutes the largest fraction of PM_{10} at roadside sites (Chow et al. 1995; Kleeman and Cass 1998; Jaecker-Voirol and Pelt 2000; Harrison et al. 2001). Dust on road surfaces is derived from a wide range of sources, including road-surface erosion and deposition of vehicle-generated PM. Emission estimates for road-surface wear (which consists principally of the erosion of bitumen-based surfaces) vary from 4 to 400 mg/vehicle km traveled (Lükewille et al. 2001; Kennedy 2003). In New Zealand, higher concentrations of Cu, Sb, As, Ba, Mo, Fe, Ni, and Zn have been reported in dusts collected from street gutters compared with dusts collected from background soil. These higher concentrations have been attributed principally to brake and tire wear (Kennedy 2003).

The inhibitor studies conducted as part of the current study provided some insight into the contribution of metals to the oxidative potential of PM_{10}. When selected PM samples were co-incubated in the synthetic RTLF with the transition-metal chelator DTPA, most of the OP^{AA} and all of the OP^{GSH} of the PM were reduced. This outcome implied that a considerable fraction of the observed oxidative potential could be attributed to redox-active metals, such as Fe, Cu, and Ni.

Co-incubation with EDTA had the opposite effect on OP^{AA}. It increased OP^{AA} in all the PM samples examined. This increase reflected the binding of EDTA to surface Fe, permitting Fe mobilization while still allowing its participation in redox reactions. This paradoxic action occurs because the EDTA molecule does not completely encapsulate the Fe molecule; the Fe is held in an open basket–like position, capable of existing as both Fe^{2+} and Fe^{3+}, and thus free to participate in oxidative reactions (Liu and Hider 2002). EDTA had the opposite effect on OP^{GSH}. Another feature of EDTA is that it is able to bind to Cu, but — unlike Fe — EDTA fully encapsulates Cu so that the Cu is not free to participate in oxidative reactions, This property demonstrates that Cu in PM_{10} drives OP^{GSH}.

Co-incubation with DES, which specifically binds to Fe^{2+} and Fe^{3+} and renders Fe redox-inactive, inhibited oxidative potential in a manner similar to DTPA, suggesting the involvement of Fe (from the mobilizable pool) in the OP^{AA} of PM_{10}. The residual activity reflected by the OP^{AA} measurements following incubation with DES can be attributed to non-metal sources (i.e., quinones and organic radicals).

Co-incubation with the free-radical scavengers SOD/CAT inhibited oxidative potential. The specific $^{\bullet}OH$ scavenger DMSO had no effect (Slivka and Cohen 1988). Co-incubation with SOD/CAT ensures that antioxidant depletion driven by the presence of $O_2^{-\bullet}$ and H_2O_2 is prevented. Contributions to the measured oxidative potential from labile pro-oxidants associated with the volatile fraction of ambient PM are unlikely to be assessed, especially in PM from archived and aged filters. Taken together, the analyses conducted in this study provided evidence that PM_{10} from brake and tire wear might contribute markedly to the oxidative potential of the ambient PM at roadside sites. To investigate this possibility further, PM_{10} emissions from vehicle exhaust, tire wear, and brake wear were modeled and used to estimate primary PM_{10} at each of the 16 sites in the study. These estimates were then compared to our measurements of oxidative potential at the 16 sites. Although the oxidative potential of PM_{10} was significantly associated with the modeled primary PM_{10}, the strong mutual correlations between the contributions of vehicle exhaust, tire wear, and brake wear to primary PM_{10} made it impossible to dissect their relative contributions to the measurements of oxidative potential.

As stated in the introduction, the synthetic RTLF assay used to quantify PM's oxidative potential measures only the oxidizing properties of PM attributable to its redox-active components (as is the case with other acellular systems, which are based on electron-spin resonance [Shi et al. 2003] or the oxidation of dithiothreitol [Cho et al. 2005]). Although these measurements provide an effective integrative summary of contributions from various redox-active components of PM, they do not reflect the latent capacity of inhaled PM to elicit cellular oxidative stress through the metabolism of PAHs (Bonvallot et al. 2001), disruption of the mitochondrial electron chain (Xia et al. 2007), or induction of inflammation by PM-associated endotoxin (Alexis et al. 2006).

Another caveat in interpreting measures of oxidative potential, as defined in this study, is that these measures are limited to PM's time-stable redox-active components (i.e., metals and quinones). Contributions to oxidative potential from labile reactive oxygen species and other transient radicals are unlikely to be assessed, especially in PM from archived filters. Although some attempts have been made to quantify these transient components (Venkatachari and Hopke 2008), it is likely that accurate assessment of their contribution to PM's oxidative potential will require real-time analyses. Notably volatile organic species have been demonstrated to elicit toxicity in numerous in vitro and in vivo experiments (Rudell et al. 1999; Seagrave et al. 2002, 2003, 2005).

In summary, in the current study a novel assay system was used to investigate the effect of changes in traffic emissions on the oxidative potential of PM_{10} collected from monitoring sites in London over a 6-year period encompassing before and after the introduction of the CCS. The assay, though based on an acellular system, was designed to replicate the type of redox chemistries likely to occur in vivo when inhaled PM interacts with antioxidants in the RTLF. Although we were unable to identify an effect of the CCS on PM's oxidative potential, significant differences were observed in measures of oxidative potential at sites throughout the city; PM from roadside sites had a higher oxidative potential than PM from urban background sites. This observation supports the wealth of information from epidemiologic studies demonstrating increased respiratory or allergic symptoms in children and adults working or residing near busy roads (Brunekreef et al. 1997; Janssen et al. 2003; Gauderman et al. 2007).

Source-apportionment modeling suggested that the measured oxidative potential was more likely to be related to primary PM_{10} emissions (i.e., vehicle exhaust, tire wear, and brake wear) at these sites than to contributions from rural background PM_{10}. It also appeared to isolate brake wear as a major contributor to the observed oxidative potential. Our studies with selected metal chelators appeared to support the hypothesis that PM's redox-active metal components (Fe, Cu, Ni, and V) contributed significantly to the observed oxidative potential. The effect of Cu, a major component of brake pads, appeared to be pronounced. Although increased concentrations were seen for a range of metals reflecting brake (Cu) and tire (Zn) wear throughout London during the 6 years of the study, the concentrations of these metals decreased at the one site examined within the CCZ, possibly reflecting the reduction of vehicle numbers within the zone.

These analyses of oxidative potential and the components of PM_{10} that contribute to it are important because they highlight the possible contribution of PM sources other than vehicle exhaust to a metric related to human health effects. Currently, there are no regulations on PM emissions from brake or tire wear, even though these emissions are likely to become more important sources of ambient PM_{10} as improved engine technologies reduce the contribution of vehicle exhaust to ambient PM_{10}.

Throughout this report, we have emphasized that our investigation of the impact of the introduction of the CCS was hampered by having samples from only one site inside the zone available to us as well as by the significant gaps in the PM_{10} filter archive for the period before the introduction of the scheme. An important, if secondary, objective was to provide a detailed spatial and temporal map of oxidative potential of PM in London for the period from 2005 to 2006. This objective has been further expanded in the HEI baseline study of the London Low-Emission Zone (Kelly et al. 2011). Ultimately, these two studies on oxidative potential provide better baseline data for answering the question of whether large-scale traffic-management schemes are effective at reducing pollutant concentrations and the oxidative potential of PM. In particular, these baseline data will be used to investigate the impact on air quality of the Western Extension of the CCZ (introduced on February 19, 2006) and the city-wide Low Emission Zone (introduced on February 4, 2008). Although the current investigation has provided information on the relationship between traffic and the composition and oxidative potential of PM, the fundamental question of whether a traffic-management scheme affects the oxidative potential of PM will be addressed in our follow-up studies.

IMPLICATIONS OF FINDINGS

1. PM_{10} samples collected in London showed oxidative activity equivalent to, and in many cases greater than that of, comparable concentrations of the positive control particles (ROFA). This highlights the potential toxicity of PM within the urban environment and the need to fully understand the basis of this activity.
2. The differences between OP^{AA} and OP^{GSH} measurements demonstrate that AA and GSH respond differently to various redox components of PM.
3. Analysis of the correlations between the oxidative potential of PM_{10} (both OP^{AA} and OP^{GSH} in samples collected in 2005) and modeled concentrations of primary PM_{10} (i.e., vehicle exhaust, tire wear, and brake wear) and rural PM_{10} revealed a strong correlation with primary PM_{10} suggesting it was strongly influenced by traffic-related components of PM. However, the lack of variation in our rural PM_{10} measurements and the correlation with total PM_{10} preclude the drawing of any strong conclusions regarding the absolute contribution of primary PM sources to the measured OP.

4. The strong mutual correlations between PM_{10} emissions from vehicle exhaust and from tire wear and brake wear precluded isolation of their individual contributions to the oxidative potential of PM_{10}. Nevertheless, the study's data provided evidence that PM from non-exhaust sources might be important contributors. This is a potentially important observation, because PM emissions from tire and brake wear are not currently regulated and the contributions of these non-exhaust emissions to ambient PM_{10} are likely to become more important as new technologies continue to reduce PM emissions in vehicle exhaust.
5. The association of PM oxidative potential with primary PM_{10}, particularly from non-exhaust sources likely to gain in significance as exhaust emissions decline, suggests that this metric should be investigated further.

A key strength of the CCS study is the combination of diverse assessment techniques, including the laboratory analysis reported here and the emissions modeling and statistical analysis reported in Part 1 of this Research Report. The results of these combined techniques provide a more complete picture of the influence of the CCS than would have been possible if just one of the assessment techniques had been used. It is recommended that future studies be strengthened through closer integration of such techniques. Data from laboratory-based toxicologic analyses, for example, could be fed back into a dispersion model to map PM toxicity across London.

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APPENDIX A. HEI Quality Assurance Statement

The conduct of this study was subjected to independent audits by Dr. Richard Kwok and Dr. James Flanagan of RTI International. Kwok and Flanagan are experts in quality assurance for air quality monitor studies and related epidemiologic studies. The audits included on-site reviews of study activities for conformance to the study protocol and standard operating procedures. The dates of the audits and the phases of the study examined are shown below.

QUALITY ASSURANCE AUDITS

December 6–8, 2006

In phase 1, the auditors conducted an on-site audit at King's College London to verify the integrity of the reported data. The audit reviewed the following study components: progress reports, personnel and staff, adequacy of equipment and facilities, internal quality assurance procedures, air quality sampling methodology, and data processing procedures. Several data points for each parameter were traced through the entire data processing sequence to verify that the described procedures had been followed and to verify the integrity of the database. The audit also included spot checks of the monitoring stations' original data record against the project database for any data transcription errors. No errors were noted.

April 3–4, 2008

In phase 2, the auditor conducted on-site audits at St. George's Hospital, London and King's College London. The auditors assessed the investigators' responses to the phase 1 audit and extended the review to the health data being compiled by investigators at St. George's Hospital.

July–August, 2009

In audit phase 3, the auditors reviewed the draft final report to ensure data issues noted earlier were addressed. No further issues were noted.

Written reports of the Quality Assurance oversight inspections were provided to the HEI project manager, who transmitted the findings to the Principal Investigator. These quality assurance oversight audits demonstrated that the study was conducted by a well-coordinated, experienced team according to the study protocol and standard operating procedures. Interviews with study personnel revealed a consistently high concern for data quality. The report appears to be an accurate representation of the study.

Richard Kwok

Richard K. Kwok, Ph.D.

Epidemiologist, Quality Assurance Officer

James B. Flanagan

James Flanagan, Ph.D.

Chemist, Quality Assurance Officer

APPENDIX B. Assessment of the Contribution of Volatile Components to the Oxidative Potential of PM

INTRODUCTION

Determinations of the oxidative potential of PM are critically dependent on samples used being representative of particles present in ambient air. To date, much of the work has been based on PM extracted from standard TEOM filters. Concern has been expressed, however, that possible losses of secondary and volatile organic species may occur as a consequence of the operational configuration of the TEOM (in which the air stream is heated to 50°C to reduce the interferences from particle-bound water and to minimize thermal expansion of the tapered element). Furthermore, monitoring systems using TEOM filters are gradually being phased out in London and replaced by the FDMS monitors, which operate at different temperatures. This experiment permits a comparison of the two methods.

In its standard configuration, the air stream passing through a TEOM is heated to 50°C to reduce interferences from particle-bound water and to minimize thermal expansion of the tapered element. Operating at this temperature has the acknowledged disadvantage of driving off ammonium nitrate and volatile organic aerosols (Rupprecht et al. 1992, Allen et al. 1997; Salter and Parsons 1999; Soutar et al. 1999; Green et al. 2001; Josef et al. 2001; Charron et al. 2004) leading to an underestimate of mass. To overcome this problem the FDMS developed by Rupprecht and Patashnick, Inc. (Albany, NY) employs a Nafion dryer bundle to remove water from the sampled air. In its operational mode, air passing the dryer is alternated (every 6 minutes) between two modes: base and purge (or reference). During the base measurement the sample flow enters the sensor directly and the microbalance, held at 30°C, detects mass changes related to the particles in the air stream together with evaporative and other artifacts. During the purge cycle, the sample flow is directed through a 47-mm filter maintained at 4°C, which retains all particles, with the ambient air continuing to the sensor, such that the microbalance for this period only measures mass attributable to artifact effects. This system therefore permits determination of the total PM mass attributable to volatile and nonvolatile sources. Several published studies have investigated the discrepancy in mass determined between parallel TEOM and FDMS monitors (Frank 2006; Schwab et al. 2006), with recent reports indicating that much of this discrepancy is accounted for by ammonium nitrate and volatile organic species (Grover et al. 2005; Schwab et al. 2006). The FDMS PM_{10} purge measurement has been shown to agree well with measurements of ammonium nitrate mass (taken with a colocated Rupprecht & Patashnick ambient particulate nitrate monitor [model 8400]) in $PM_{2.5}$ at sites in London, explaining approximately 50% of the mass differential between FDMS and TEOM filters (Green 2005).

To address whether volatile PM components contribute significantly to PM oxidative potential, a comparability study was performed examining PM_{10} oxidative potential in samples collected in parallel using a standard TEOM or the FDMS. In FDMS samplers the microbalance measures the mass of a dehumidified sample at 30°C (base concentration) before switching the sample stream through an additional filter chilled to 4°C (purge concentration). Thus PM trapped on filters collected at these varying temperatures should retain differing amounts of organic components and ammonium nitrate permitting the contribution of these volatile species to the oxidative activity of PM_{10} to be assessed.

RESULTS AND DISCUSSION

A comparison of PM_{10} oxidative potential of samples from colocated FDMS and TEOM samplers was conducted. Eleven parallel purge (4°C) and base (30°C) FDMS filters were obtained from the K & C—North Kensington monitoring station (urban background) covering the period of March 15, 2005, to May 10, 2006, (4-week collections). Ten more parallel FDMS purge and base filters were obtained from Westminster—Marylebone Road (roadside), again reflecting 4-week collections over the period of March 16, 2005, to April 12, 2006. A number of the collected filters were not included in the full analysis due to inconsistencies in time and date labeling. In addition to the FDMS samples, parallel TEOM filters were obtained from both sites; 7 and 8 from the K & C—North Kensington and Westminster—Marylebone sites, respectively. At the K & C—North Kensington sampling site the available TEOM filters covered equivalent periods to the FDMS purge and base filters, whereas at Westminster—Marylebone site two to four separate TEOM filters covered each of the FDMS sampling periods. Hence the TEOM antioxidant data presented reflect the mean value of the individual filters collected and analyzed over this period. The relatively few parallel TEOM filters reflect the unavailability of validated masses for some of the later collection periods or inconsistencies in the sample labeling, which prevented accurate pairing of the samples. For the Westminster—Marylebone Road site, TEOM-derived values were only included in the analysis when extracts from all of the filters covering the FDMS sampling window were available.

The results of the analyses on paired filter extracts from the TEOM and FDMS purge and base filters are presented in Figure B.1. Comparisons between the oxidative activities of the PM extracted from each filter were analyzed using a one-way ANOVA. Where significant differences (< 5% at the 95% confidence level) were noted in either

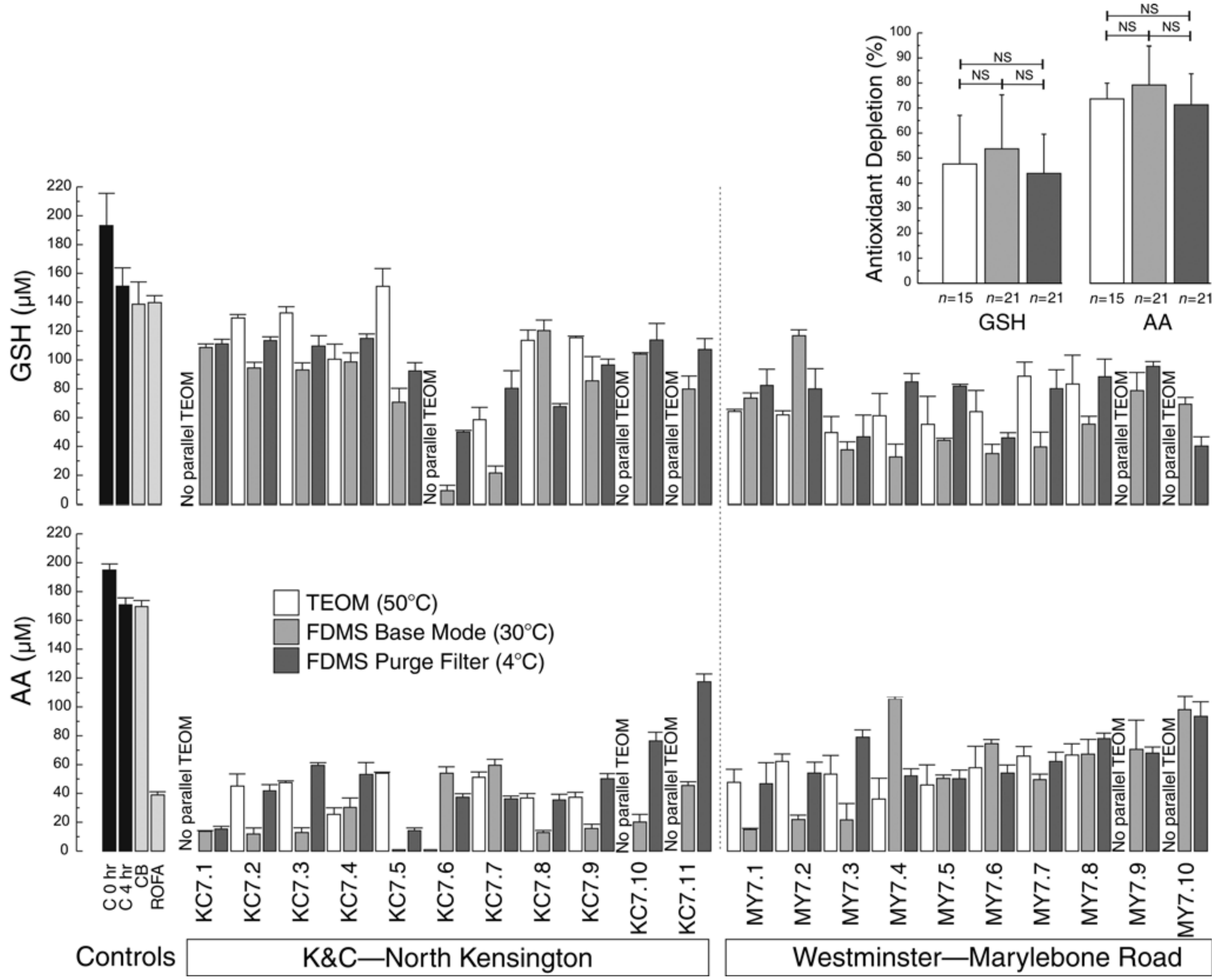

Figure B.1. AA and GSH concentrations remaining after a 4-hour incubation of 50 μg/mL PM_{10} in synthetic RTLF: comparison of samples from colocated TEOM and FDMS monitors. PM_{10} was extracted from TEOM filters (white bars) and from FDMS base filters (light gray bars) and FDMS purge filters (dark gray bars) from colocated TEOM and FDMS monitors at K & C—North Kensington and Westminster—Marylebone Road. The individual paired data from all of the filters collected are shown as the mean ± 1 SD of triplicate incubations. Antioxidant concentrations in particle-free controls before and after a 4-hour incubation period (C 0 hr and C 4 hr, respectively), the negative control (CB), and the positive control (ROFA) are shown. Missing filters are indicated. The inset panel shows the mean percentage depletion of AA and GSH in all paired TEOM and FDMS samples. Comparisons were performed using a one-way ANOVA with post hoc testing using paired *t* tests. To allow for multiple comparisons, a Bonferroni correction was applied, with $P < 0.017$ considered significant.

the AA or GSH data sets, analysis between the groups of paired filters was performed using paired *t* tests applying a Bonferroni correction for multiple comparisons. Using these criteria, $P < 0.017$ was considered statistically significant. Although there was evidence of significant differences between the parallel filter extracts in their capacity to deplete GSH from the synthetic RTLF ($P = 0.01$, determined by ANOVA), the individual group differences failed to attain statistical significance, with only a suggestive trend of reduced activity in the FDMS purge extract compared with PM extracted from the base filter ($P = 0.022$). No quantitative differences were noted in the capacity of PM extracts obtained from any of the filter types to deplete AA from the synthetic RTLF.

Although no statistical differences were apparent between the mean oxidative potential values determined for the PM samples collected at 50°C, 30°C, and 4°C, the correlations between the extent of PM-induced antioxidant oxidation observed with the parallel FDMS base and purge filters illustrated in Figure B.2 were poor. Weak associations for both AA ($r^2 = 0.15$, $P = 0.08$) and GSH depletion ($r^2 = 0.31$, $P < 0.01$) were observed between PM_{10} extracted

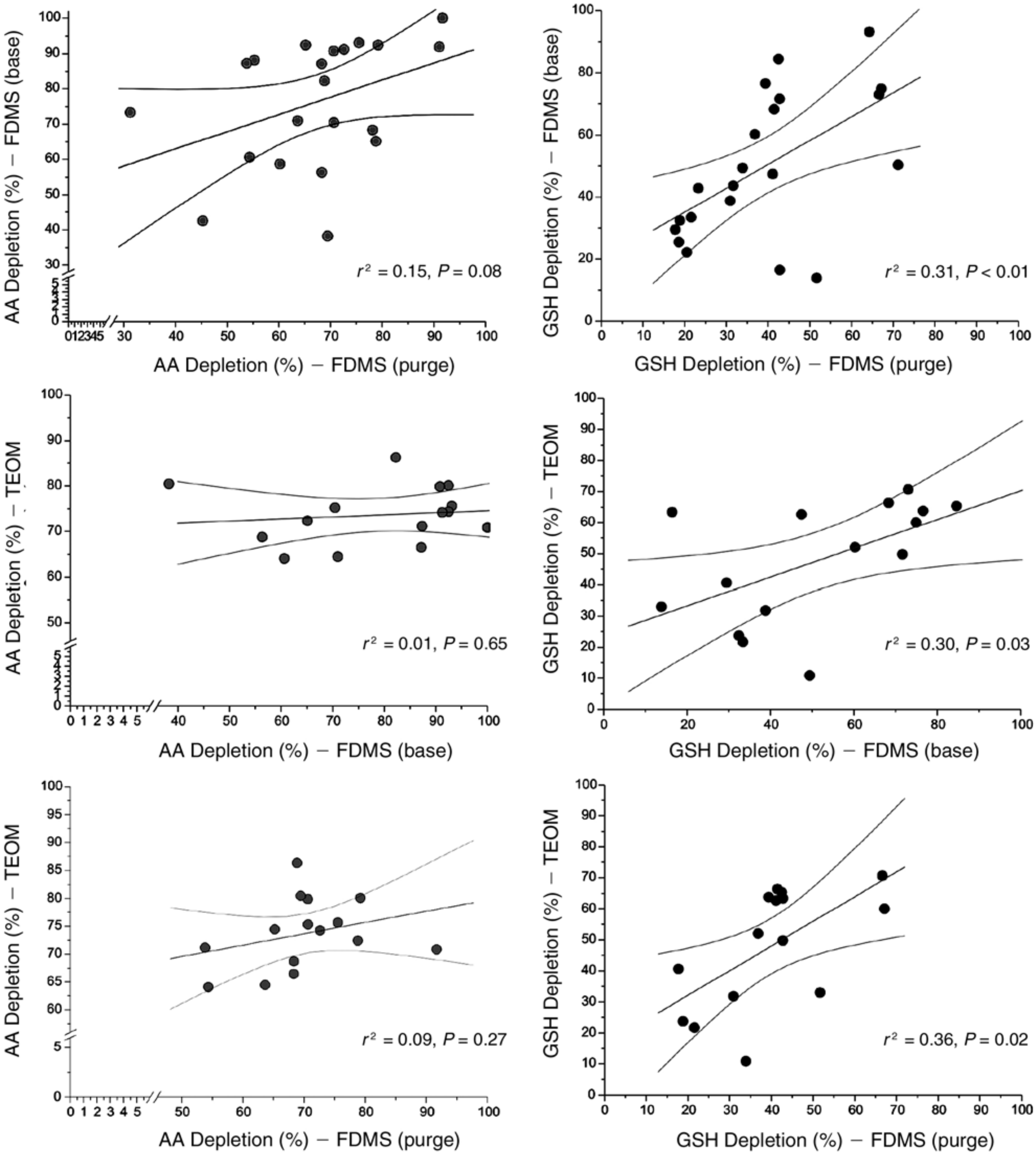

Figure B.2. Associations between PM_{10} oxidative potentials of extracts from paired TEOM and FDMS filters. Oxidative potential was expressed as the percentage depletion of AA or GSH from synthetic RTLF after a 4-hour incubation. Both base and purge FDMS filters are compared. Details of a linear regression through the data set are shown with 95% confidence intervals.

from parallel purge and base FDMS filters. GSH depletion by PM extracted from TEOM filters showed significant association with that observed from both the base ($r^2 = 0.30$, $P = 0.03$) and purge ($r^2 = 0.36$, $P = 0.02$) FDMS collections. No such associations were noted when AA depletion was considered (Figure B.2).

This poor agreement in oxidative potential measured in parallel PM samples collected by TEOM and FDMS was concerning and could not be explained by uncertainty in the assessment of the oxidative potential of PM. A previous comparison of the oxidative potential of PM samples collected from TEOM and FDMS monitor systems, which used parallel monitors at two sites in the U.K., also showed poor agreement in oxidative potential measures made with parallel TEOM and FDMS samplers (Mudway 2004). In this study two TEOM and FDMS monitors were deployed at each site; the repeatability of the oxidative potential measurements could thus be established using each collection system. This study indicated good agreement for parallel TEOM filters; values of paired samples fell on the line of identity and had associated low uncertainties (3.12 and 3.04 µM for AA and GSH, respectively, based on a starting concentration of 200 µM). In contrast, the repeatability of measurements of oxidative potential of PM samples collected on paired purge and base filters from the FDMS was poor. At this time the investigators remain uncertain and concerned about the variability observed with FDMS filters, which is why they focused on TEOM-derived PM in the current study. The investigators would therefore contend that much of the variability seen between TEOM and FDMS filter–derived PM oxidative activities in this study reflect uncertainties associated with the latter PM sampling technique.

APPENDIX C. PM Oxidative Potential Measurements

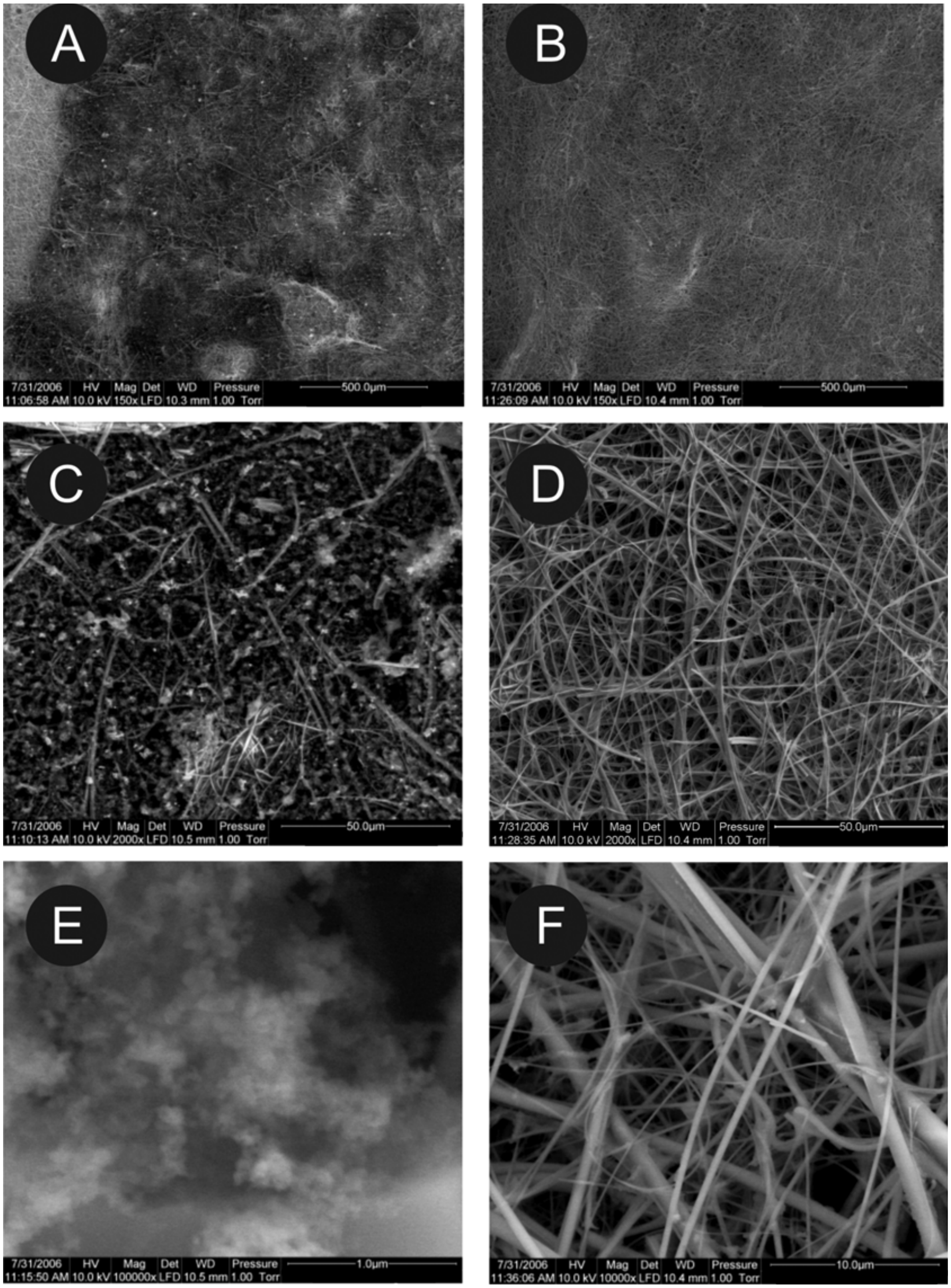

Figure C.1. Scanning EM images of FDMS PM_{10} filters from Westminster—Marylebone Road site. Panels **A, C,** and **E** show micrographs of filters before extraction (8/31/2004). Panels **B, D,** and **F** show micrographs of filters after extraction process (3/9/2005). Original magnifications: **A,** 150×; **B,** 150×; **C,** 2000×; **D,** 2000×; **E,** 100,000×; and **F,** 10,000×.

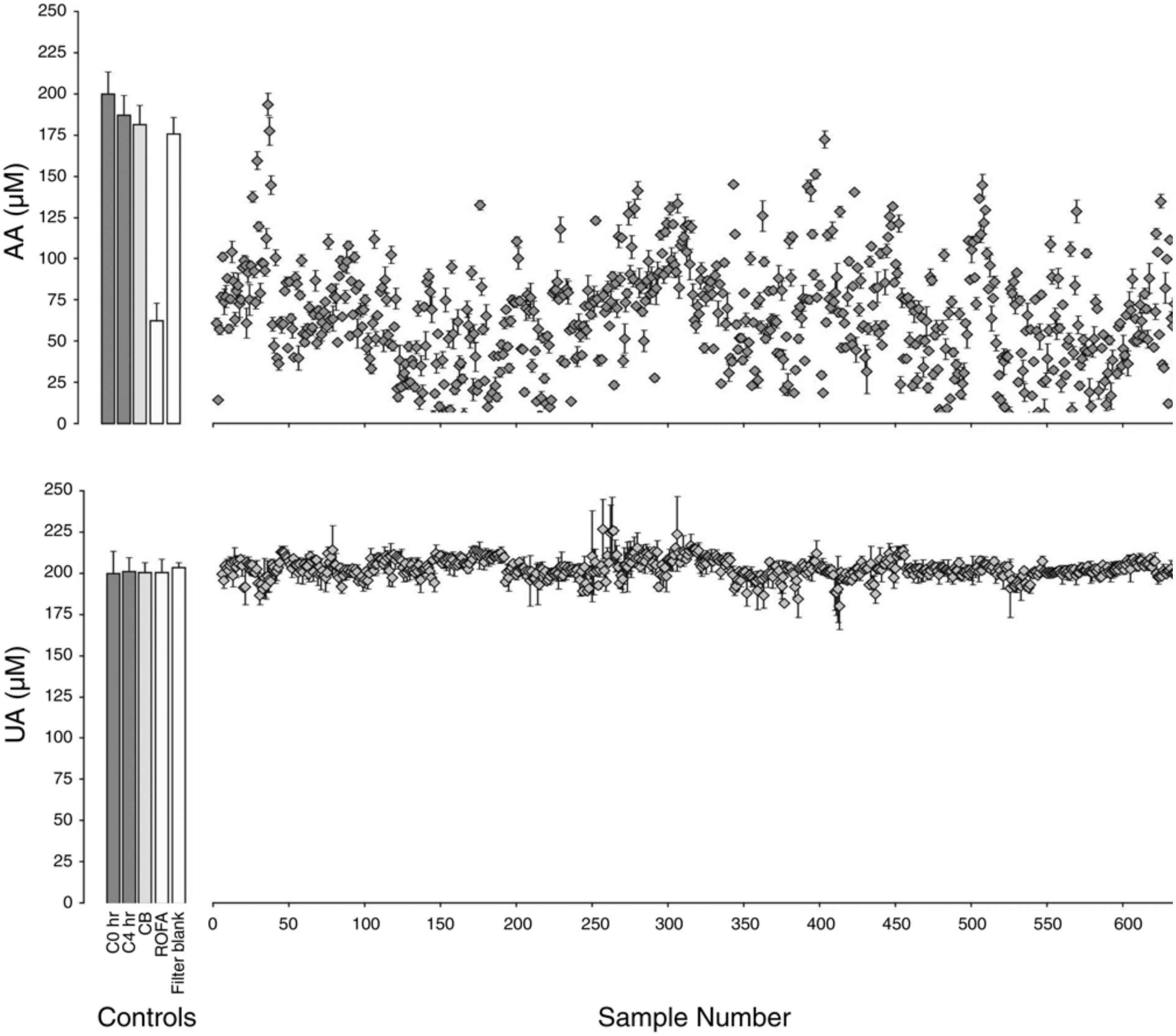

Figure C.2. Concentrations of AA and UA remaining in the synthetic RTLF after a 4-hour incubation of ~ 730 TEOM PM_{10} filter extracts and control particles at a concentration of 50 µg/mL PM_{10}. The sample number indicates the sequence in which the samples were analyzed. Each point represents the mean (± 1 SD) antioxidant concentration following incubation with each of the PM samples in triplicate. AA and UA concentrations at the beginning (C 0 hr) and end (C 4 hr) of the 4-hour incubation in the absence of particles are illustrated, together with the concentrations remaining after the 4-hour incubation with negative and positive control particles, CB and ROFA, respectively (bars). In addition, antioxidant losses associated with extracts from blank TEOM filters are shown.

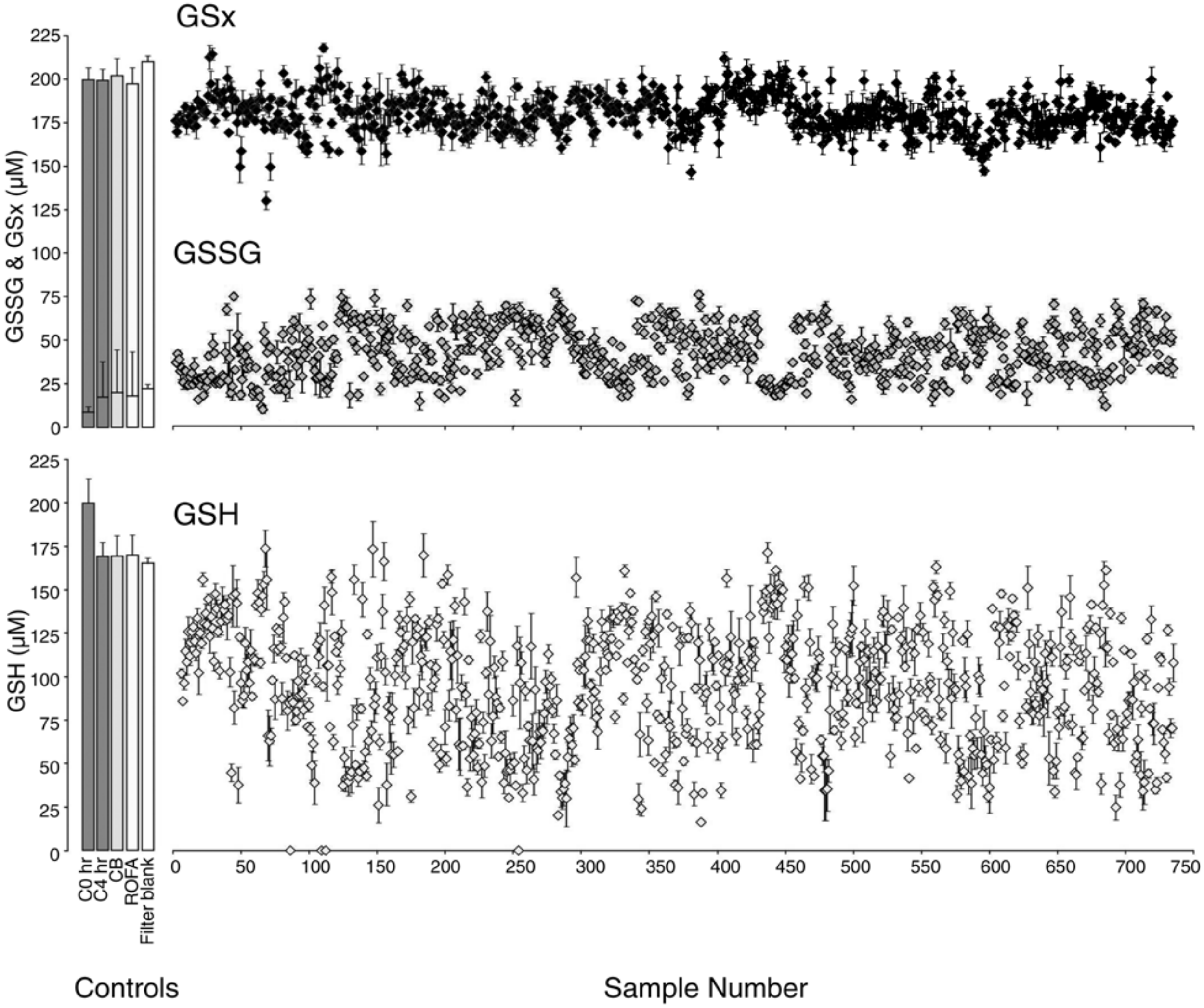

Figure C.3. Concentrations of total (GSx), oxidized (GSSG), and reduced (GSH) glutathione remaining in synthetic RTLF after 4-hour incubation with 50 μg/mL PM_{10}. For details see Figure C.2 caption.

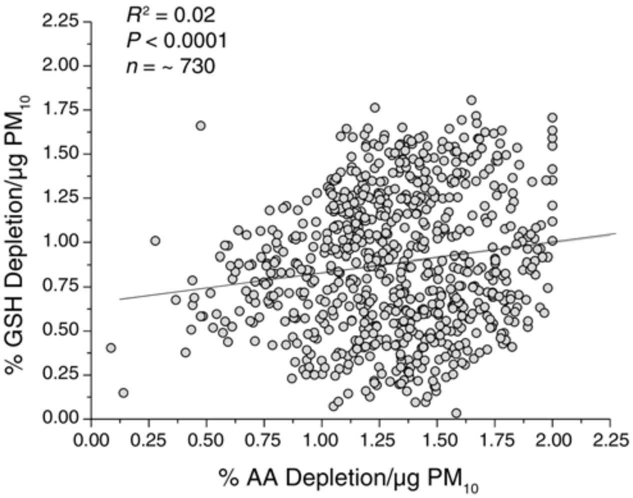

Figure C.4. The associations between the extent of depletion of AA and GSH in samples from individual filter extracts ($n = \sim 730$). Data are expressed as percentage depletion per µg PM_{10} (compared with the particle-free control) after a 4-hour incubation. Each point represents the mean of triplicate determinations. The results of a linear regression analysis are shown.

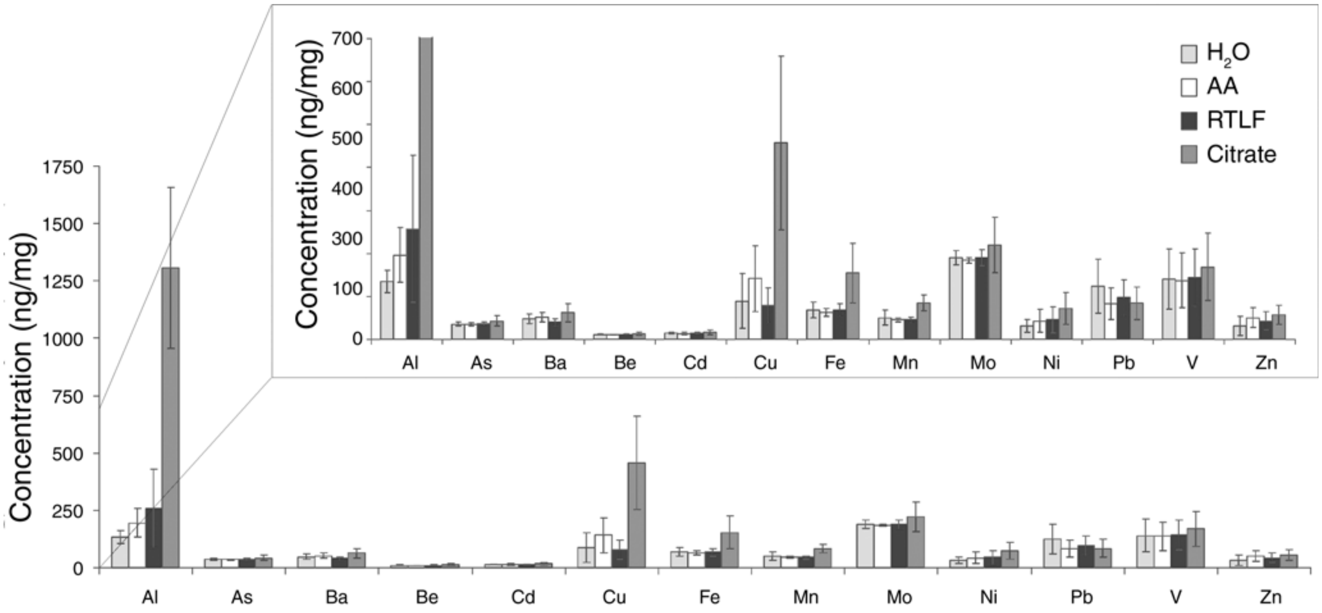

Figure C.5. Metal concentrations after a 4-hour incubation in ultrapure, Chelex-100 resin–treated water, AA (200 µM), synthetic RTLF (200 µM AA, UA, and GSH) or citrate (1 mM). All incubation media were pH 7.0. Data represent the means ± 1 SD of 12 PM samples. The inset panel highlights the concentrations of the low-abundance metals.

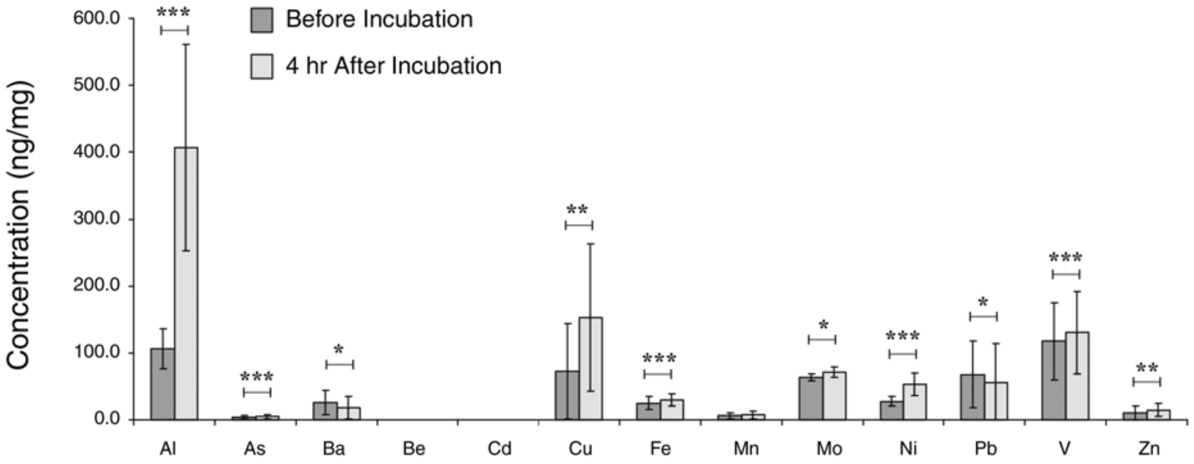

Figure C.6. Comparison of metal concentrations mobilized from the surface of PM samples before and after a 4-hour incubation in synthetic RTLF. Data represent the means ± 1 SD of 12 separate PM samples. Comparison of concentrations before and after incubation was performed using a paired *t* test. Statistical differences were shown as follows: $^*P < 0.05$, $^{**}P < 0.01$, $^{***}P < 0.001$ (two-tailed).

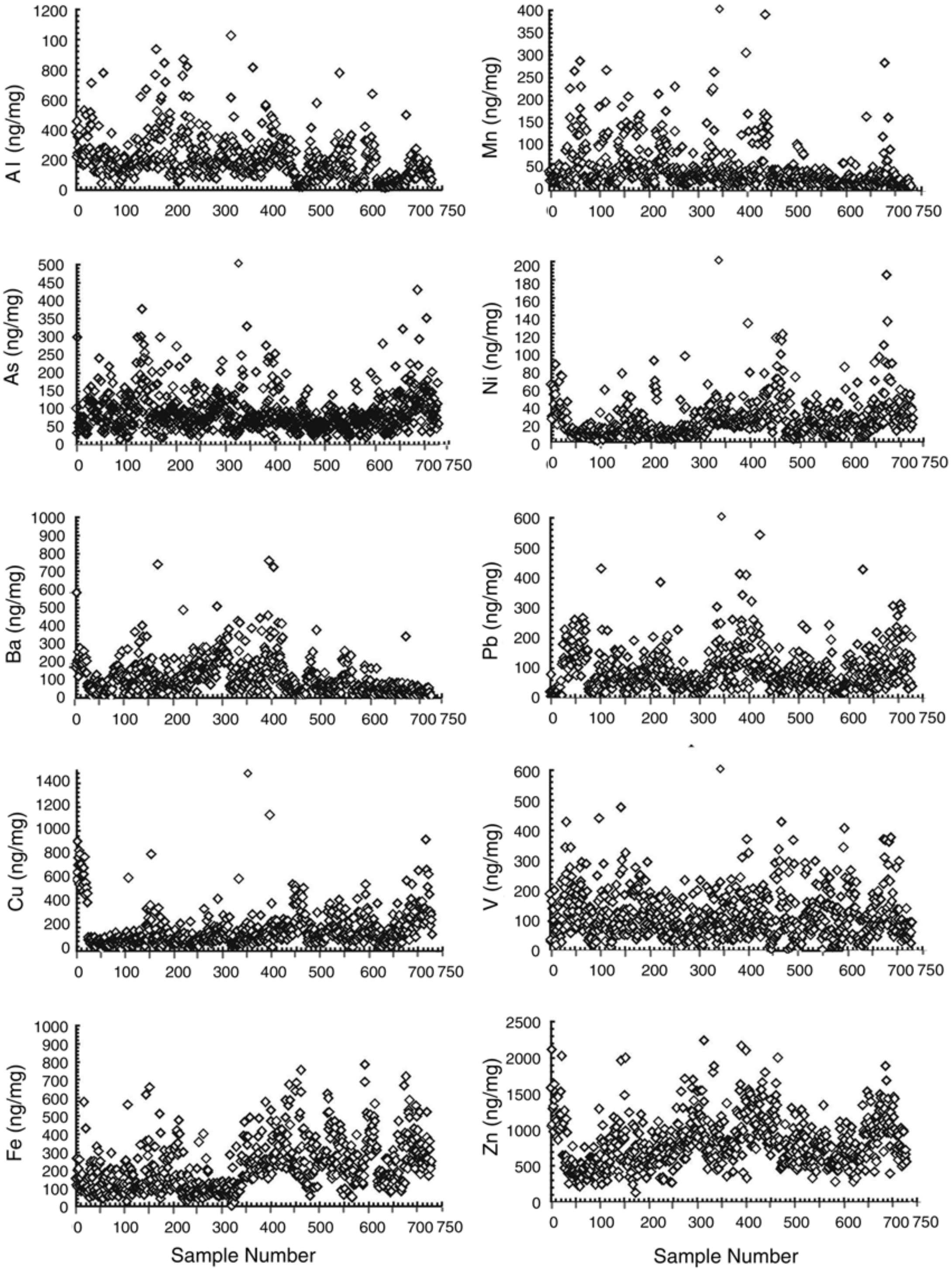

Figure C.7. Aqueous metal concentrations in ~ 730 PM_{10} filter extracts. Data are illustrated as the means of triplicate readings on a single sample. Note differences in *y*-axis scales.

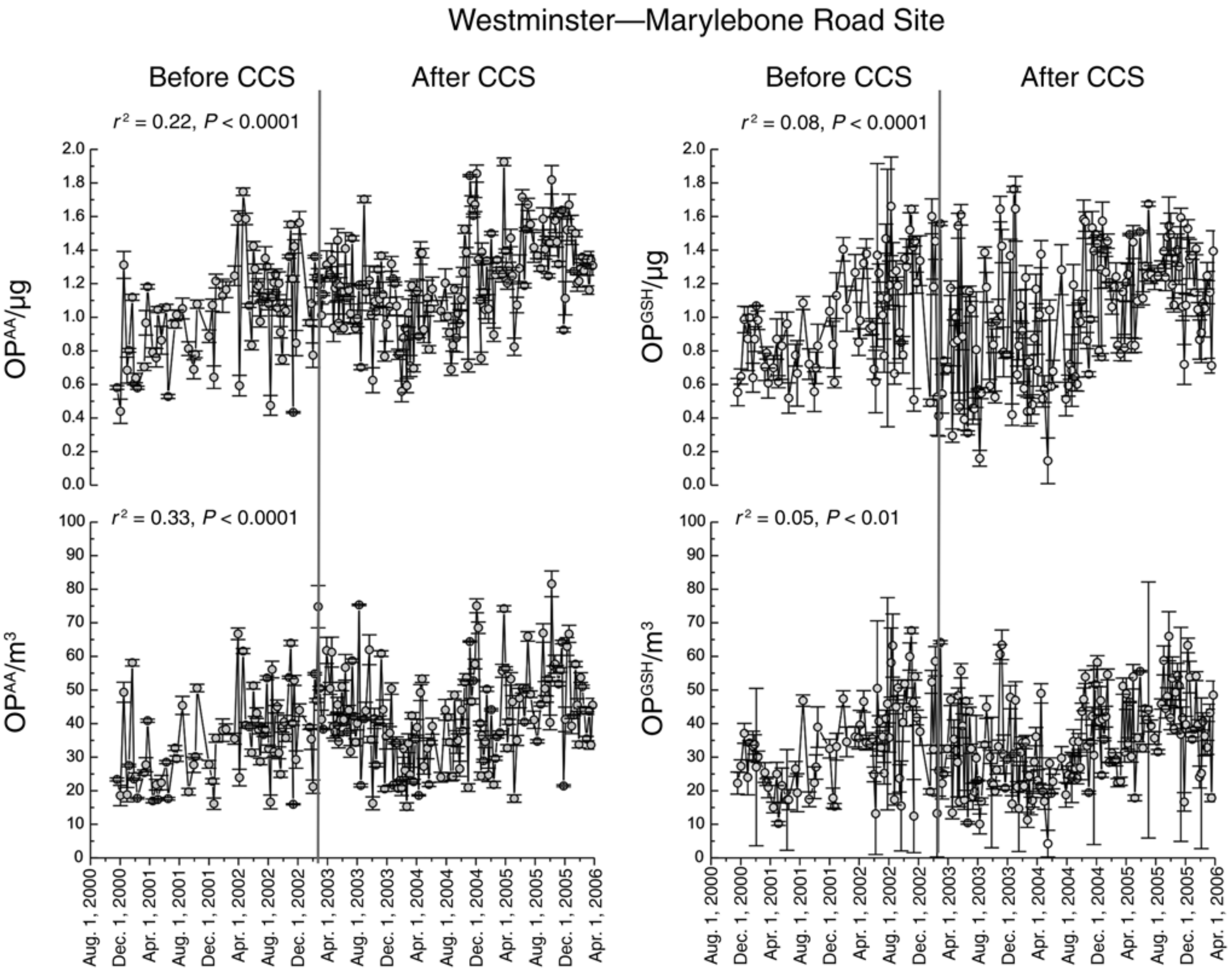

Figure C.8. Temporal patterns of two metrics for OP^{AA} and OP^{GSH} for PM collected at the roadside Westminster—Marylebone Road site before and after the CCS. Samples were collected from November 15, 2000, to March 29, 2006. OP^{AA} and OP^{GSH} are expressed per µg of extracted PM_{10} or per m^3 of sampled air. Each data point represents the mean ± 1 SD of triplicate incubations, with the value of the oxidative potential plotted to the midpoint of the sampled interval. The vertical line in each panel indicates the date the CCS was introduced. The results of linear regression analyses through these four data sets are shown.

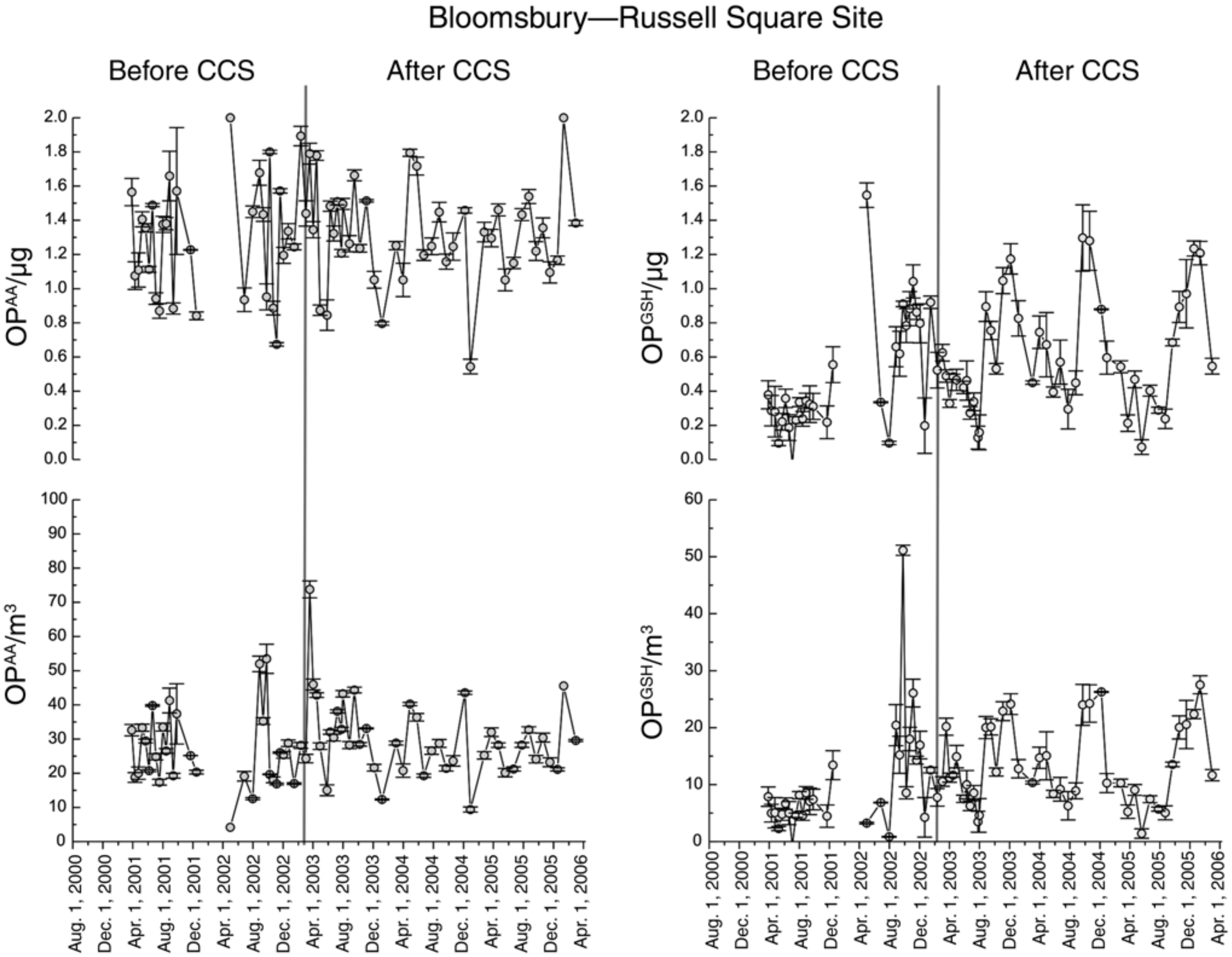

Figure C.9. Temporal patterns of two metrics for OP^{AA} and OP^{GSH} for PM collected at the urban background Bloomsbury—Russell Square site before and after CCS. Samples were collected from March 21, 2001, to March 3, 2006. OP^{AA} and OP^{GSH} are expressed per µg of extracted PM_{10} or per m^3 of sampled air. See Figure C.8 for additional details.

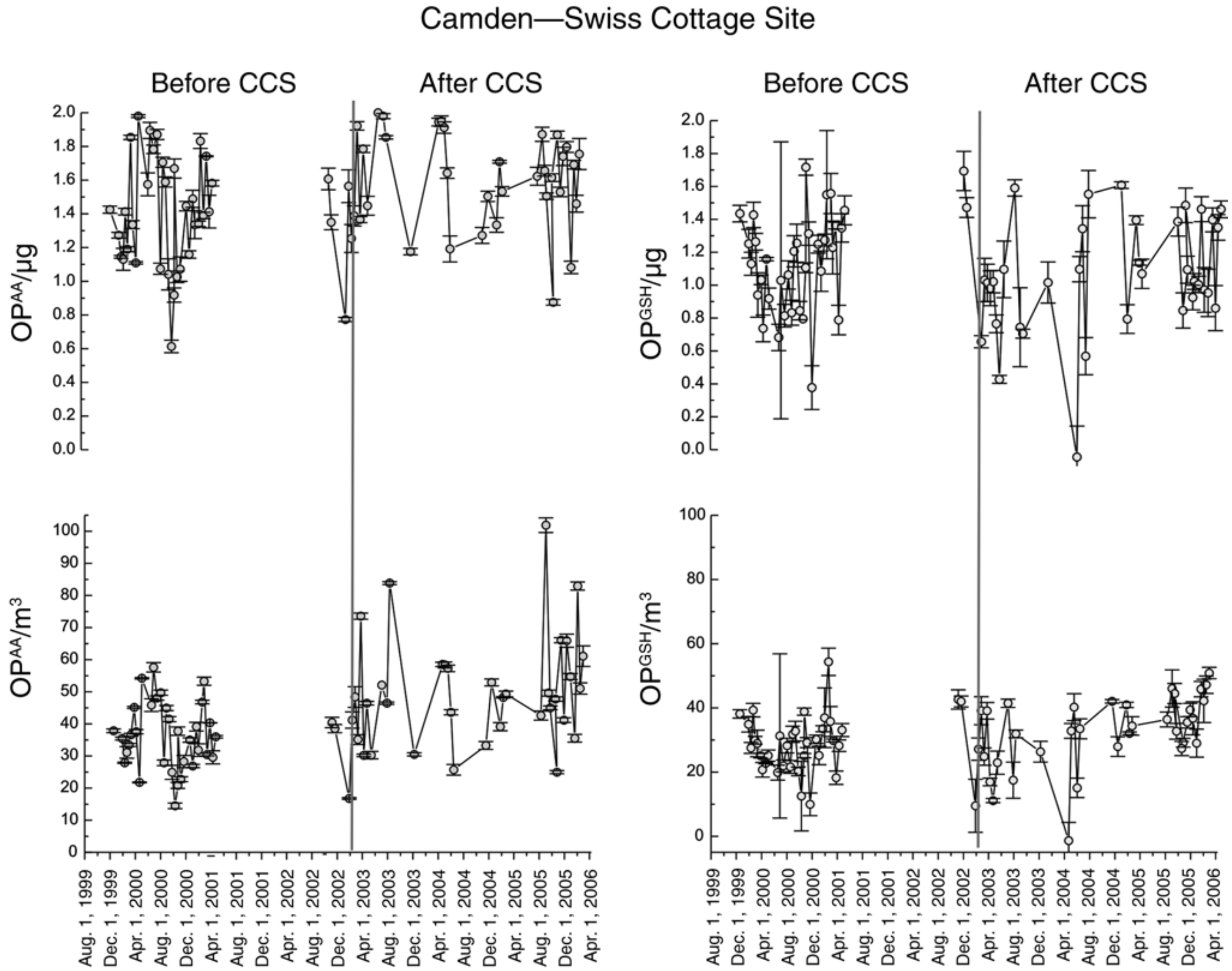

Figure C.10. Temporal patterns of two metrics for OP^{AA} and OP^{GSH} for PM collected at the roadside Camden—Swiss Cottage site before and after CCS. Samples were collected from December 14, 1999, to March 9, 2006. OP^{AA} and OP^{GSH} are expressed per µg of extracted PM$_{10}$ or per m^3 of sampled air. See Figure C.8 for additional details.

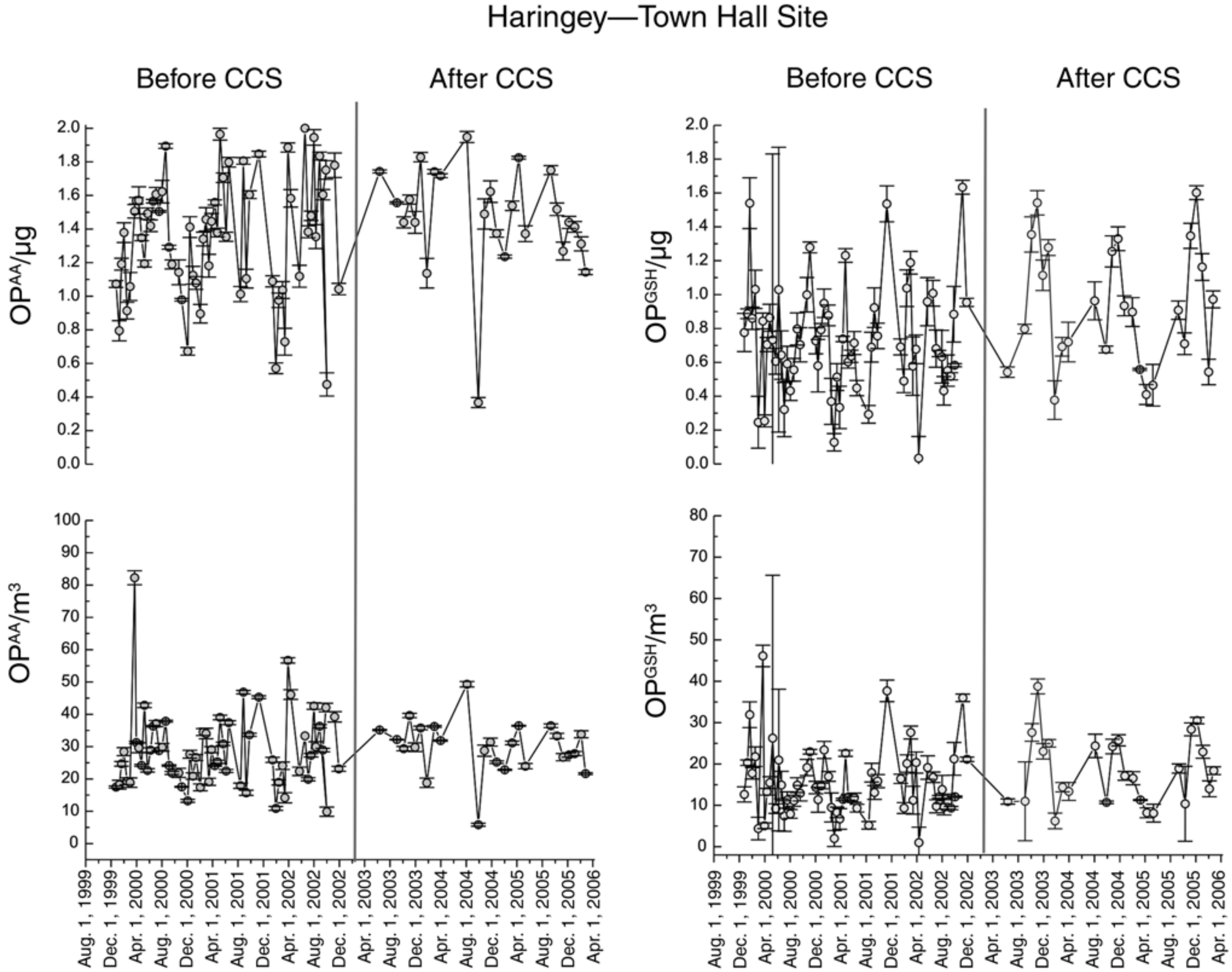

Figure C.11. Temporal patterns of two metrics for OP^{AA} and OP^{GSH} for PM collected at the roadside Haringey—Town Hall site before and after CCS. Samples were collected from December 14, 1999, to March 6, 2006. OP^{AA} and OP^{GSH} are expressed per µg of extracted PM_{10} or per m^3 of sampled air. See Figure C.8 for additional details.

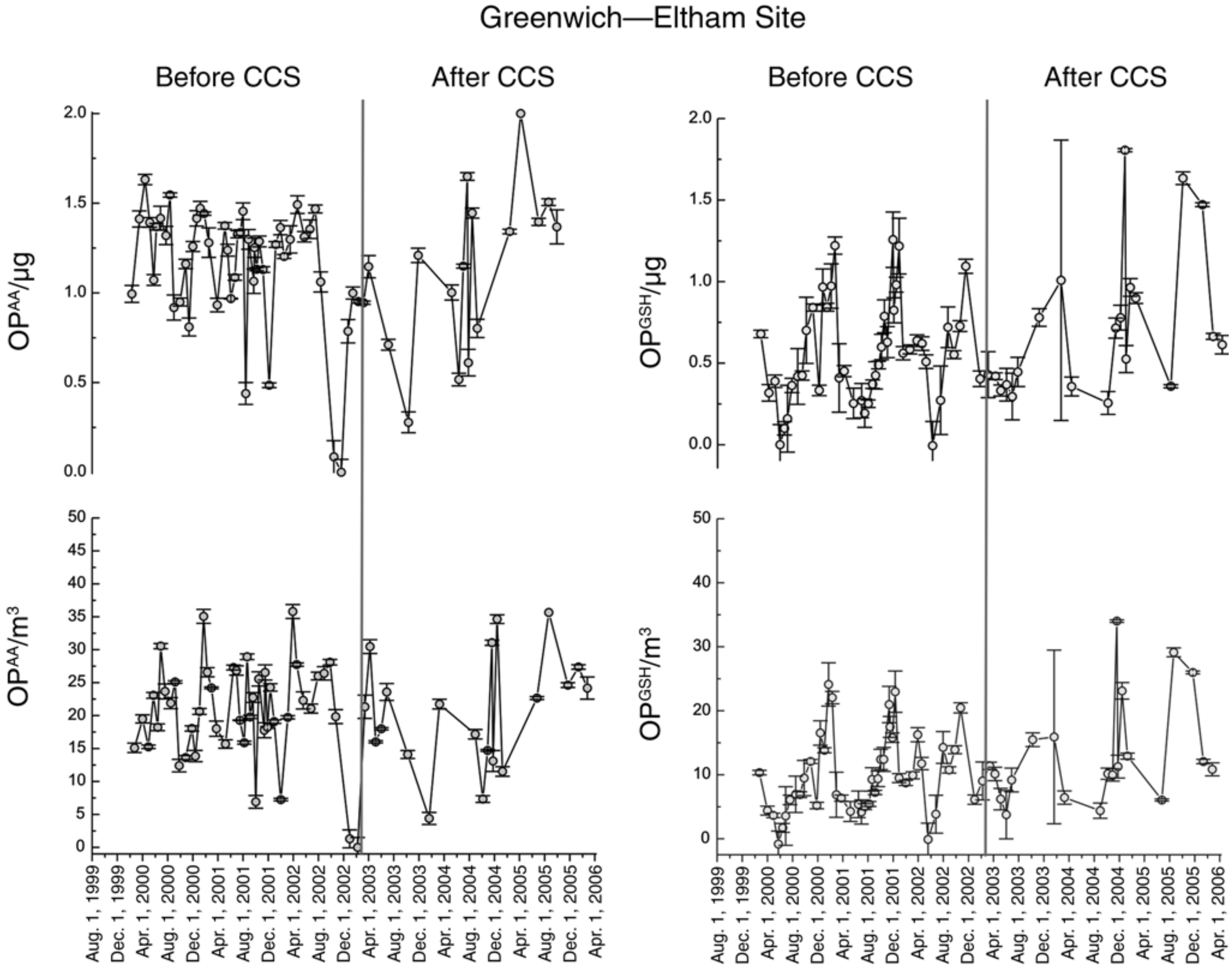

Figure C.12. Temporal patterns of two metrics for OP^{AA} and OP^{GSH} for PM collected at the urban background Greenwich—Eltham site. Samples were collected from January 1, 2000, to March 17, 2006. OP^{AA} and OP^{GSH} are expressed per μg of extracted PM$_{10}$ or per m^3 of sampled air. See Figure C.8 for additional details.

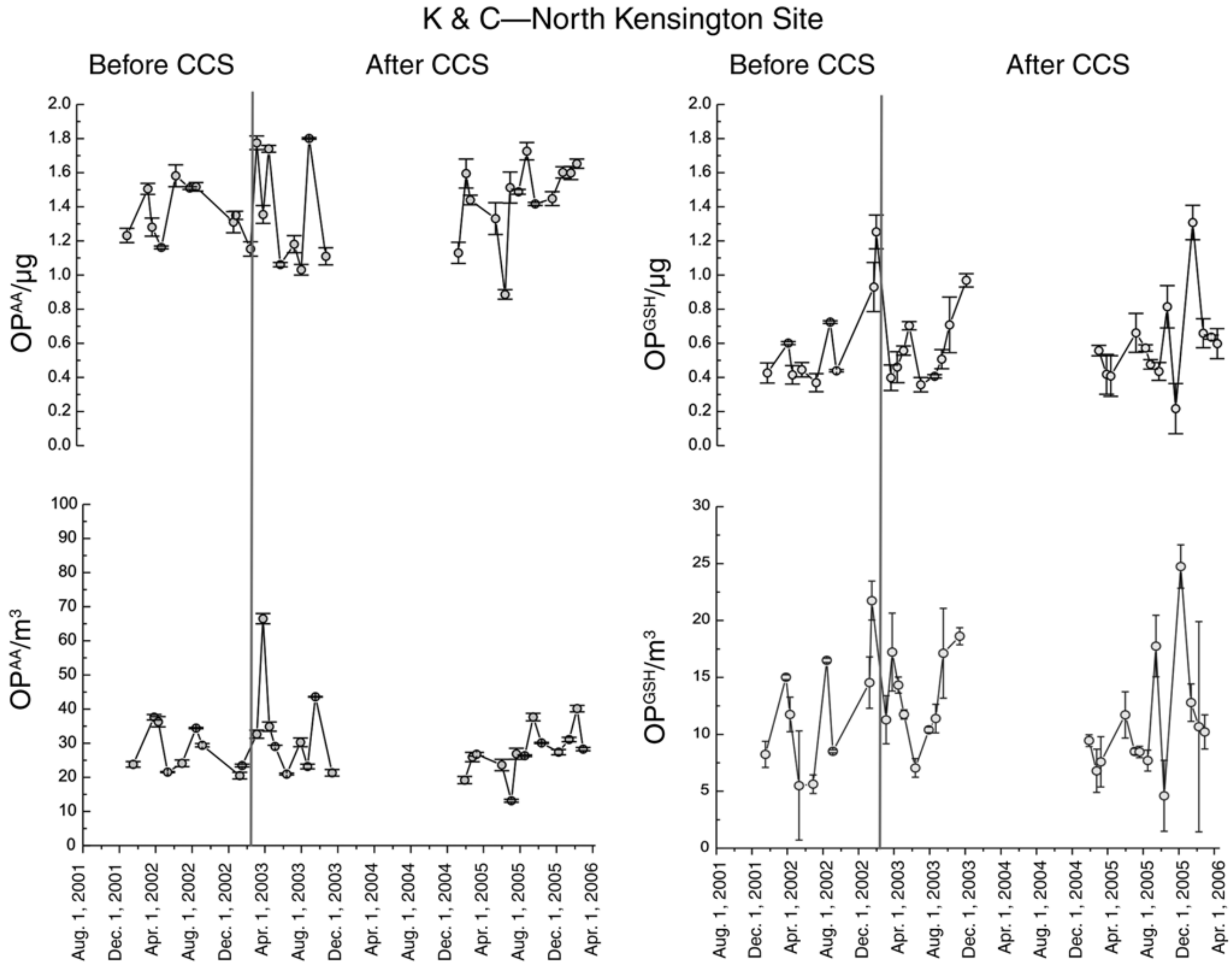

Figure C.13. Temporal patterns of two metrics for OP^{AA} and OP^{GSH} for PM collected at the urban background K & C—North Kensington site. Samples were collected from January 9, 2002, to March 13, 2006. OP^{AA} and OP^{GSH} are expressed per μg of extracted PM_{10} or per m^3 of sampled air. See Figure C.8 for additional details.

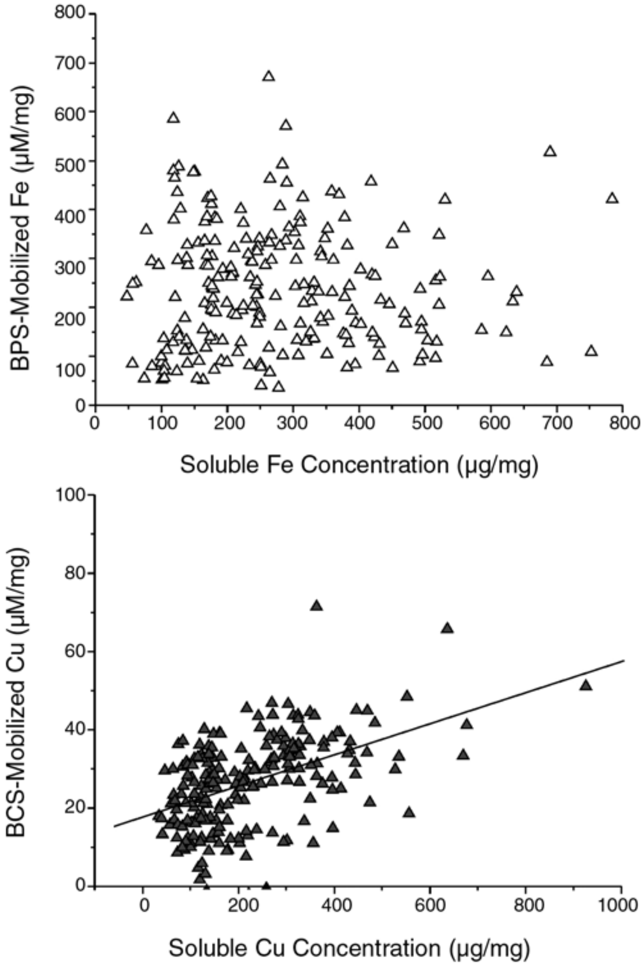

Figure C.14. Associations between mobilized and aqueous Fe and Cu. Concentrations of BPS-mobilized bioavailable Fe (Fe^{2+}/Fe^{3+}), aqueous Fe, BCS-mobilized Cu (Cu^{+}/Cu^{2+}), and aqueous Cu concentrations were determined by ICP–MS. The linear regression analysis of the Cu data set showed $r^2 = 0.22$. Each data point represents the mean of triplicate determinations. PM_{10} samples were collected from each of the 16 sites between December 2004 and April 2006.

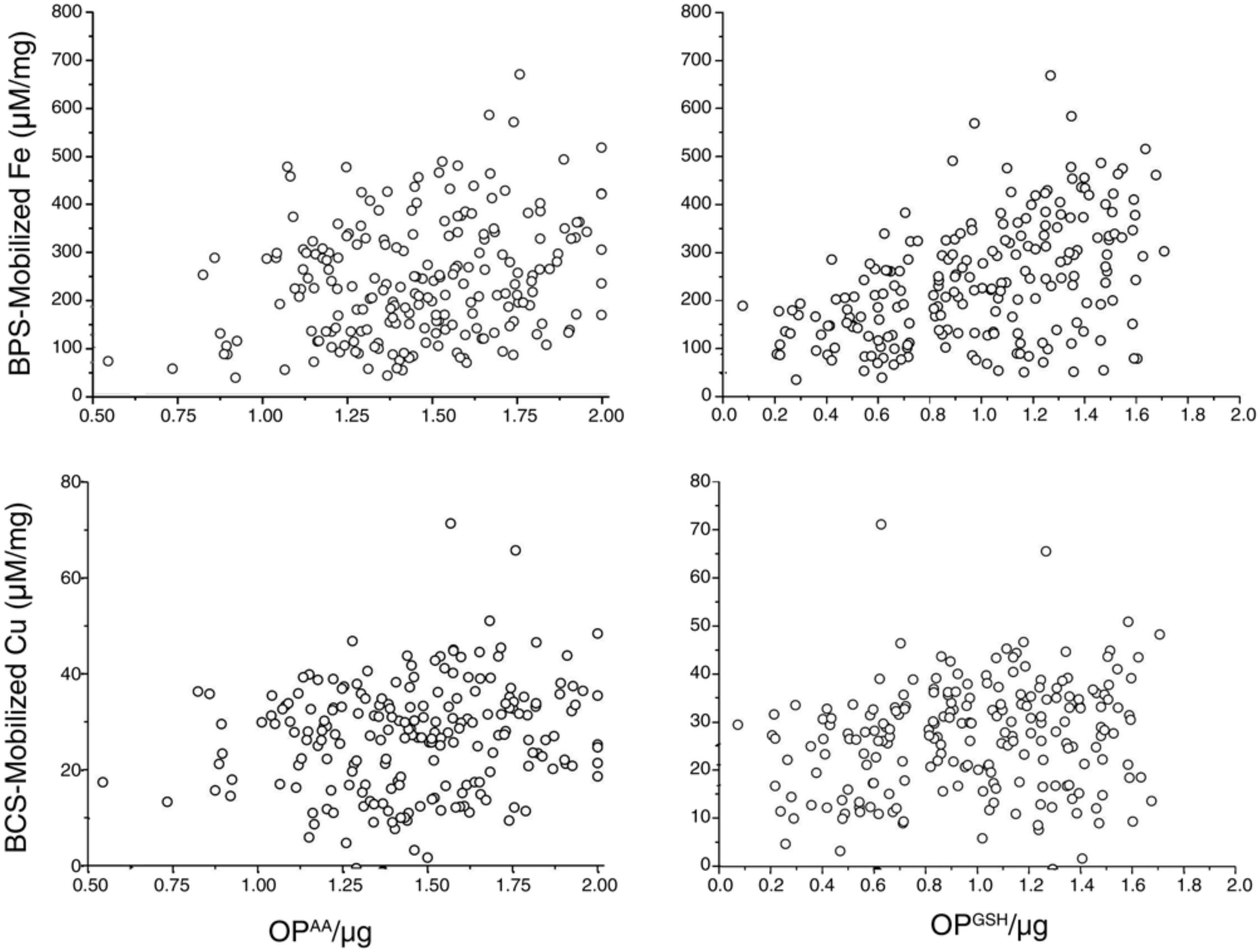

Figure C.15. Associations between BPS-mobilized Fe (Fe^{2+}/Fe^{3+}) or BCS-mobilized Cu (Cu^{+}/Cu^{2+}) concentrations with OP^{AA} and OP^{GSH} (expressed per µg of extracted PM_{10}). Each data point represents the mean of triplicate determinations. Bioavailable Fe and Cu were determined on PM_{10} samples collected from each of the 16 sites between December 2004 and April 2006.

Table C.1. Descriptive Data on Oxidative Potential and Metal Components of PM_{10}

Parameter (units)	*n*[a]	Mean (95% CI)	Skewness	Kurtosis
PM_{10} (%/μg)	729	26.25 (25.65 to 26.87)	0.85	0.92
OP^{AA}/μg (μg/μg)	729	1.31 (1.29 to 1.34)	−0.38	0.23
OP^{AA}/m^3 (%/m^3)	729	34.30 (33.30 to 35.31)	0.73	1.12
OP^{GSH}/μg (μg/m^3)	729	0.88 (0.85 to 0.91)	0.09	−0.83
OP^{GSH}/m^3 (%/m^3)	729	23.5 (22.5 to 24.5)	0.61	−0.22
Al (ng/mg)	728	207.0 (191.8 to 222.7)	7.71	103.41
As (ng/mg)	728	92.18 (88.10 to 96.2)	1.85	4.93
Ba (ng/mg)	728	113.0 (105.9 to 120.0)	2.23	8.31
Cu (ng/mg)	728	175.1 (164.3 to 185.9)	2.32	6.77
Fe (ng/mg)	728	220.0 (208.0 to 231.5)	3.02	21.53
Mn (ng/mg)	728	47.4 (43.7 to 51.2)	3.77	23.83
Mo (ng/mg)	728	33.3 (18.0 to 84.7)	27.00	729.39
Ni (ng/mg)	728	25.3 (23.7 to 26.9)	3.21	17.07
Pb (ng/mg)	728	91.5 (86.6 to 96.3)	1.93	6.40
V (ng/mg)	728	119.6 (113.6 to 125.6)	2.20	12.37
Zn (ng/mg)	728	833.3 (806.9 to 859.7)	1.22	2.92

[a] Approximately 730 PM_{10} samples were analyzed in a blinded fashion. Upon unblinding the sample codes it was apparent that three of the samples had collection periods that overlapped with other samples. After reviewing the data it was decided that this reflected labeling errors by the site operators and these samples were excluded from all subsequent analyses.

Table C.2. Descriptive Data on Copollutants and Site Temperature[a]

Parameter (Units)	*n*	Mean (95% CI)	Skewness	Kurtosis
NO (μg/m^3)	690	60.10 (56.49 to 63.70)	1.00	0.62
NO_x (μg/m^3)	701	95.47 (90.89 to 100.04)	0.82	−0.09
NO_2 (μg/m^3)	692	36.02 (34.86 to 37.18)	0.70	−0.17
CO (μg/m^3)	415	0.79 (0.75 to 0.84)	1.21	1.83
SO_2 (μg/m^3)	591	2.85 (2.73 to 2.97)	1.29	2.72
O_3 (μg/m^3)	408	11.50 (10.80 to 12.20)	0.81	0.03
$PM_{2.5}$ (μg/m^3)	218	17.20 (16.53 to 17.88)	0.96	1.62
Temperature (°C)	707	11.94 (11.55 to 12.33)	0.20	1.01

[a] Data collected over the same time period as PM_{10} filter collection.

Table C.3. Associations Between Measures of Oxidative Potential Using PM_{10} Mass (µg PM_{10}) and Concentrations (ng/mg) of Aqueous Metals Found in PM_{10}[a]

Site (n)	Code	Al	As	Ba	Cu	Fe	Mn	Ni	Pb	V	Zn
OP^{AA}/µg											
All Sites (728)		0.067	0.162	0.021	0.304	0.457	0.199	0.223	0.077	0.374	0.09
Bloomsbury—Russell Square (71)	BL0	0.321***	0.209	0.245*	0.360**	0.519**	0.378**	0.251*	−0.102	0.599**	0.229
Westminster—Marylebone Road (212)	MY1	−0.137*	0.183**	−0.043	0.111	0.271**	0.036	0.147*	0.001	0.292**	−0.038
Camden—Swiss Cottage (71)	CD1	0.017	0.058	0.034	0.499**	0.451**	0.059	0.333**	−0.417**	0.335**	0.246**
Haringey—Town Hall (87)	HG1	0.411**	0.285**	0.465**	0.600**	0.510**	0.340**	0.521**	−0.198	0.591**	0.425**
K & C—North Kensington (31)	KC1	0.102	0.512**	0.068	0.696**	0.720**	−0.038	0.105	0.596**	0.484**	0.273
Greenwich—Eltham (65)	GR4	−0.01	0.204	−0.109	0.216	0.550**	0.258*	−0.026	0.195	0.361**	−0.010
Brent—Kingsbury (13)	BT1	−0.088	0.220	0.275	0.126	0.346	0.379	0.047	−0.110	0.269	0.203
Camden—Shaftesbury Avenue (11)	CD3	−0.155	0.082	−0.427	0.291	0.355	0.145	0.369	0.127	0.155	0.464
K & C—Cromwell Road (28)	KC2	0.054	0.054	−0.001	0.126	0.241	0.271	0.037	−0.027	0.125	0.158
Southwark—Elephant & Castle (18)	SK1	0.084	−0.364	−0.053	−0.007	0.430	0.067	−0.224	−0.212	0.362	−0.340
Southwark—Old Kent Road (28)	SK2	0.080	−0.111	0.218	0.074	0.319	0.398*	0.130	−0.475*	0.637**	−0.148
Lewisham—New Cross (12)	LW2	−0.210	0.007	0.091	0.168	0.503	0.175	0.350	−0.287	0.678*	−0.315
H & F—Broadway (32)	HF1	0.301	−0.042	0.187	0.095	0.173	0.466**	0.198	−0.186	0.207	0.266
H & F—Brook Green (13)	HF2	0.148	0.016	−0.220	−0.038	0.236	0.011	−0.121	−0.055	0.077	0.374
Richmond—Castelnau (20)	RI1	0.051	0.380	0.422	0.412	0.341	0.562**	0.322	0.008	0.538*	0.421
Wandsworth—High Street (17)	WA4	0.265	0.118	0.076	0.363	0.456	0.412	0.194	−0.042	0.561*	−0.049

Table continues next page

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[a] Associations are Spearman rank order correlations. Oxidative potential is derived from measures of depletion of an antioxidant, AA or GSH, indicated by OP^{AA} or OP^{GSH}, respectively, per µg of PM_{10}. Data are from approximately 730 samples collected from 16 sites and correlations were calculated for the entire set of samples and for subsets by site. *P* values for the entire data set are not shown because of potential clustering by site. ** and * indicate that the associations observed at a given site were significant at $P < 0.01$ and $P < 0.05$, respectively (using a two-tailed test).

Table C.3 (*Continued*). Associations Between Measures of Oxidative Potential Using PM_{10} Mass (µg PM_{10}) and Concentrations (ng/mg) of Aqueous Metals Found in PM_{10}[a]

Site (*n*)	Code	Al	As	Ba	Cu	Fe	Mn	Ni	Pb	V	Zn
OP^{GSH}/µg											
All sites (728)		−0.300	0.212	0.263	0.109	−0.305	−0.314	−0.244	−0.141	−0.374	0.013
Bloomsbury—Russell Square (71)	BL0	−0.391**	0.511**	−0.012	0.002	−0.441**	−0.434**	−0.183	0.237*	−0.071	−0.100
Westminster—Marylebone Road (212)	MY1	−0.415**	0.177**	−0.134	−0.318**	−0.105	−0.285**	−0.334**	0.066	−0.123	−0.355**
Camden—Swiss Cottage (71)	CD1	0.018	0.316**	0.149	0.013	−0.340**	−0.059	−0.120	0.147	−0.222	0.109
Haringey—Town Hall (87)	HG1	0.024	0.387**	0.247*	0.081	−0.390**	−0.243*	−0.006	0.312**	−0.197	0.240*
K & C—North Kensington (31)	KC1	−0.210	0.619**	0.260	0.489**	0.112	−0.157	0.336	0.359*	0.358*	0.298
Greenwich—Eltham (65)	GR4	−0.307*	0.640**	0.181	0.207	−0.290*	−0.173	−0.041	0.442**	−0.389**	0.243
Brent—Kingsbury (13)	BT1	0.016	0.467	0.478	0.308	−0.203	0.280	0.083	0.159	−0.423	0.412
Camden—Shaftesbury Avenue (11)	CD3	−0.527	0.000	−0.027	−0.082	−0.309	−0.091	−0.050	−0.191	−0.264	−0.427
K & C—Cromwell Road (28)	KC2	−0.220	−0.380*	−0.128	−0.431*	−0.508**	−0.499**	−0.452*	−0.308	−0.363	−0.589**
Southwark—Elephant & Castle (18)	SK1	−0.133	0.439	−0.187	−0.172	−0.348	−0.049	−0.373	0.201	−0.616**	−0.057
Southwark—Old Kent Road (28)	SK2	−0.368	0.651**	−0.045	0.135	−0.660**	−0.299	−0.278	0.267	−0.510**	0.247
Lewisham—New Cross (12)	LW2	−0.434	0.503	−0.252	0.664*	−0.538	−0.483	0.210	0.371	−0.483	0.203
H & F—Broadway (32)	HF1	−0.175	0.612**	−0.102	−0.026	−0.338	−0.358*	0.011	0.138	−0.239	0.084
H & F—Brook Green (13)	HF2	−0.253	0.698**	0.121	0.231	−0.253	−0.703**	−0.072	0.736**	−0.610*	0.264
Richmond—Castelnau (20)	RI1	0.036	0.907**	0.391	0.299	−0.295	0.012	−0.021	0.546*	0.105	0.293
Wandsworth—High Street (17)	WA4	0.074	0.652**	0.299	−0.042	−0.338	−0.137	0.129	0.252	−0.245	0.118

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[a] Associations are Spearman rank order correlations. Oxidative potential is derived from measures of depletion of an antioxidant, AA or GSH, indicated by OP^{AA} or OP^{GSH}, respectively, per µg of PM_{10}. Data are from approximately 730 samples collected from 16 sites and correlations were calculated for the entire set of samples and for subsets by site. *P* values for the entire data set are not shown because of potential clustering by site. ** and * indicate that the associations observed at a given site were significant at $P < 0.01$ and $P < 0.05$, respectively (using a two-tailed test).

Table C.4. Associations Between Measures of Oxidative Potential (OP^{AA}/m^3 or OP^{GSH}/m^3) and Concentrations of Copollutants (µg/m^3) and Temperature (^{o}C) [a]

Site	Code	NO	NO_2	NO_x	CO	SO_2	O_3	PM_{10}	$PM_{2.5}$	Temperature
OP^{AA}/m^3										
All Sites		0.457 (689)	0.563 (691)	0.499 (700)	0.286 (415)	0.337 (591)	−0.399 (408)	0.720 (711)	0.804 (218)	0.061 (707)
Bloomsbury—Russell Square	BL0	0.061 (53)	0.226 (53)	0.140 (65)	0.147 (71)	0.284* (71)	0.020 (70)	0.642** (54)	0.729** (71)	0.100 (69)
Westminster—Marylebone Road	MY1	0.213** (210)	0.525** (210)	0.316** (210)	0.012 (212)	0.202** (209)	−0.217** (212)	0.665** (212)	0.759** (146)	0.152* (204)
Camden—Swiss Cottage	CD1	0.159 (55)	0.508** (58)	0.251 (55)	—	—	—	0.805** (70)	—	0.099 (68)
Haringey—Town Hall	HG1	0.202 (86)	0.494** (86)	0.299** (86)	—	0.411** (86)	—	0.757** (86)	—	0.199 (80)
K & C—North Kensington	KC1	0.348 (31)	0.654** (31)	0.488** (31)	0.156 (31)	0.649** (31)	−0.055 (31)	0.849** (31)	—	−0.073 (29)
Greenwich—Eltham	GR4	0.218 (65)	0.177 (65)	0.218 (65)	—	0.369** (65)	−0.054 (65)	0.530** (65)	—	0.143 (64)
Brent—Kingsbury	BT1	0.228 (13)	0.357 (13)	0.274 (13)	−0.275 (12)	0.991 (13)	−0.044 (13)	0.547 (13)	—	−0.127 (13)
Camden—Shaftesbury Avenue	CD3	0.271 (10)	0.231 (10)	0.268 (10)	—	—	—	0.574 (11)	—	0.070 (11)
K & C—Cromwell Road	KC2	0.358 (28)	0.387* (28)	0.371 (28)	0.311 (28)	0.661** (28)	—	0.780** (28)	—	0.177 (28)
Southwark—Elephant & Castle	SK1	0.186 (18)	0.285 (18)	0.218 (18)	0.070 (18)	0.520* (18)	0.128 (16)	0.671** (18)	—	0.107 (18)
Southwark—Old Kent Road	SK2	0.413* (27)	0.372 (26)	0.418* (26)	0.250 (26)	0.244 (26)	—	0.730** (28)	—	0.015 (28)
Lewisham—New Cross	LW2	−0.599 (11)	−0.451 (11)	−0.603 (11)	—	−0.003 (12)	—	0.325 (12)	—	0.420 (12)
H & F—Broadway	HF1	0.379* (32)	0.364* (32)	0.389* (32)	—	0.388* (31)	—	0.704** (32)	—	0.125 (32)
H & F—Brook Green	HF2	−0.019 (13)	0.119 (13)	0.519 (13)	—	—	—	0.725** (13)	—	0.275 (13)
Richmond—Castelnau	RI1	0.324 (20)	0.323 (20)	0.335 (20)	—	—	—	0.616** (20)	—	0.063 (20)
Wandsworth—High Street	WA4	0.499* (17)	0.667** (17)	0.562* (17)	0.583* (17)	—	—	0.536* (17)	—	−0.004 (17)

Table continues next page

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[a] Associations are expressed as Pearson correlation coefficients. Numbers of samples are shown in parentheses. Oxidative potential is derived from measures of depletion of AA or GSH in the synthetic RTLF assay and expressed as OP per m^3 of sampled air indicated by OP^{AA}/m^3 or OP^{GSH}/m^3, respectively. ** and * indicate that the associations observed at a given site were significant at $P < 0.01$ 0.01 and $P < 0.05$, respectively (using a two-tailed test).

Table C.4 (*Continued*). Associations Between Measures of Oxidative Potential (OP^{AA}/m^3 or OP^{GSH}/m^3) and Concentrations of Copollutants (μg/m^3) and Temperature (°C) [a]

Site	Code	NO	NO_2	NO_x	CO	SO_2	O_3	PM_{10}	$PM_{2.5}$	Temperature
OP^{GSH}/m^3										
All Sites		0.699 (689)	0.699 (691)	0.717 (700)	0.538 (415)	0.336 (591)	−0.655 (408)	0.654 (711)	0.519(218)	0.061 (707)
Bloomsbury—Russell Square	BL0	0.500** (53)	0.508** (53)	0.471** (65)	0.041 (71)	−0.002 (71)	−0.462** (70)	−0.027 (54)	0.199 (71)	−0.328** (69)
Westminster—Marylebone Road	MY1	0.336** (210)	0.387** (210)	0.386** (210)	0.132 (212)	0.134 (209)	−0.426** (212)	0.310** (212)	0.264** (146)	0.026 (204)
Camden—Swiss Cottage	CD1	0.254 (55)	0.488** (58)	0.326* (55)	—	—	—	0.418** (70)	—	−0.234 (68)
Haringey—Town Hall	HG1	0.572** (86)	0.437** (86)	0.566** (86)	—	0.348** (86)	—	0.467** (86)	—	−0.174 (80)
K & C—North Kensington	KC1	0.561** (31)	0.446* (31)	0.546** (31)	0.347 (31)	0.396* (31)	−0.346 (31)	0.271 (31)	—	−0.228 (29)
Greenwich—Eltham	GR4	0.639** (65)	0.542** (65)	0.646** (65)	—	0.059 (65)	−0.636** (65)	0.244** (65)	—	−0.431** (64)
Brent—Kingsbury	BT1	0.931** (13)	0.669* (13)	0.913** (13)	0.569 (12)	0.306 (13)	−0.801 (13)	−0.031 (13)	—	−0.226 (13)
Camden—Shaftesbury Avenue	CD3	−0.339 (10)	−0.338 (10)	−0.342 (10)	—	—	—	−0.371 (11)	—	0.444 (11)
K & C—Cromwell Road	KC2	−0.090 (28)	−0.156 (28)	−0.105 (28)	−0.188 (28)	−0.233 (28)	—	0.159 (28)	—	0.477* (28)
Southwark—Elephant & Castle	SK1	0.692** (18)	0.689** (18)	0.710** (18)	0.753** (18)	0.213 (18)	−0.671** (16)	0.545* (18)	—	−0.540* (18)
Southwark—Old Kent Road	SK2	0.859** (27)	0.817** (26)	0.876** (26)	0.689** (26)	0.280 (26)	—	0.584** (28)	—	−0.551 (28)
Lewisham—New Cross	LW2	0.590 (11)	0.029 (11)	0.438 (11)	—	0.359 (12)	—	0.189 (12)	—	−0.137 (12)
H & F—Broadway	HF1	0.737** (32)	0.632** (32)	0.740** (32)	—	0.478* (31)	—	0.465** (32)	—	−0.274 (32)
H & F—Brook Green	HF2	0.893** (13)	0.500 (13)	0.829** (13)	—	—	—	0.362 (13)	—	−0.188 (13)
Richmond—Castelnau	RI1	0.717** (20)	0.448* (20)	0.673** (20)	—	—	—	0.361 (20)	—	−0.154 (20)
Wandsworth—High Street	WA4	0.498* (17)	0.418 (17)	0.486* (17)	0.574* (17)	—	—	0.450 (17)	—	0.065 (17)

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[a] Associations are expressed as Pearson correlation coefficients. Numbers of samples are shown in parentheses. Oxidative potential is derived from measures of depletion of AA or GSH in the synthetic RTLF assay and expressed as OP per m^3 of sampled air indicated by OP^{AA}/m^3 or OP^{GSH}/m^3, respectively. ** and * indicate that the associations observed at a given site were significant at $P < 0.01$ 0.01 and $P < 0.05$, respectively (using a two-tailed test).

Table C.5. Associations Between Measures of Oxidative Potential Using PM_{10} Mass (OP^{AA}/µg PM_{10} or OP^{GSH}/µg PM_{10}) and Concentrations (ng/mg PM_{10}) of Aqueous Metals Found in PM_{10} Samples Collected from December 2004 to March 2006[a]

Site (*n*)	Code	Al	As	Ba	Cu	Fe	Mn	Ni	Pb	V	Zn
OP^{AA}/µg											
Bloomsbury—Russell Square (14)	BL0	0.235	0.301	−0.156	0.736**	0.644*	0.767**	0.551*	0.007	0.701**	0.473
Westminster—Marylebone Road (55)	MY1	0.008	0.197	−0.128	0.212	0.220	−0.106	0.010	−0.128	0.167	−0.126
Camden—Swiss Cottage (17)	CD1	−0.199	0.181	0.056	−0.017	0.054	0.233	−0.053	0.020	0.039	0.000
Haringey—Town Hall (12)	HG1	0.056	0.105	0.098	0.350	0.371	0.580*	0.357	−0.734**	0.699*	0.084
K & C—North Kensington (13)	KC1	0.071	0.390	−0.170	0.500	0.231	−0.181	0.110	0.214	0.170	−0.060
Greenwich—Eltham (6)	GR4	0.371	0.771	0.086	1.000**	0.600	0.657	0.486	−0.029	0.600	0.714
Brent—Kingsbury (8)	BT1	−0.310	0.524	0.619	0.262	0.310	0.667	0.072	0.048	0.333	0.357
Camden—Shaftesbury Avenue (11)	CD3	−0.155	0.082	−0.427	0.291	0.355	0.145	0.369	0.127	0.155	0.464
K & C—Cromwell Road (21)	KC2	−0.016	−0.234	−0.043	0.325	0.508*	0.330	0.198	−0.168	0.318	0.166
Southwark—Elephant & Castle (14)	SK1	0.437	−0.187	0.363	0.385	0.705**	0.389	0.073	0.037	0.556*	−0.121
Southwark—Old Kent Road (24)	SK2	0.228	−0.281	0.411*	0.124	0.528**	0.569**	0.279	−0.587**	0.780**	0.037
Lewisham—New Cross (12)	LW2	−0.210	0.007	0.091	0.168	0.503	0.175	0.350	−0.287	0.678*	−0.315
H & F—Broadway (26)	HF1	0.235	−0.136	0.207	0.213	0.300	0.509**	0.358	−0.158	0.312	0.356
H & F—Brook Green (11)	HF2	−0.223	0.005	−0.492	0.232	0.688*	0.214	0.400	−0.023	0.328	0.437
Richmond—Castelnau (16)	RI1	0.103	0.429	0.515*	0.468	0.599*	0.712**	0.556*	0.050	0.559*	0.509*
Wandsworth—High Street (11)	WA4	0.147	0.081	−0.103	0.393	0.657*	0.582*	0.253	−0.073	0.754**	−0.292
OP^{GSH}/µg											
Bloomsbury—Russell Square (14)	BL0	−0.763**	0.789**	−0.574*	0.209	−0.266	−0.411	0.139	0.262	−0.209	0.292
Westminster—Marylebone Road (55)	MY1	−0.177	−0.037	−0.356**	0.200	−0.162	−0.337*	0.049	−0.509**	0.158	−0.269*
Camden—Swiss Cottage (17)	CD1	−0.032	0.429	0.145	0.309	0.191	0.238	0.329	−0.012	0.096	0.424
Haringey—Town Hall (12)	HG1	−0.434	0.587*	−0.259	0.133	−0.552	−0.685*	−0.070	0.252	−0.469	0.336
K & C—North Kensington (13)	KC1	−0.319	0.187	−0.440	0.192	−0.148	−0.577*	0.192	0.071	0.088	−0.203
Greenwich—Eltham (6)	GR4	0.200	0.771	0.771	0.543	0.029	0.086	0.143	−0.029	0.029	0.600
Brent—Kingsbury (8)	BT1	0.190	0.714*	0.095	0.405	−0.024	0.095	0.204	−0.024	−0.238	0.238
Camden—Shaftesbury Avenue (11)	CD3	−0.220	−0.380	−0.128	−0.431*	−0.508**	−0.499**	−0.452*	−0.308	−0.363	−0.589**
K & C—Cromwell Road (21)	KC2	−0.309	−0.447*	−0.200	−0.683**	−0.700**	−0.517*	−0.625**	−0.410	−0.401	−0.666**
Southwark—Elephant & Castle (14)	SK1	−0.218	0.829**	−0.235	−0.112	−0.398	0.086	−0.402	0.437	−0.591*	0.051
Southwark—Old Kent Road (24)	SK2	−0.447*	0.612**	−0.283	0.310	−0.610**	−0.271	−0.204	0.323	−0.549**	0.187
Lewisham—New Cross (12)	LW2	−0.434	0.503	−0.252	0.664*	−0.538	−0.483	0.210	0.371	−0.483	0.203
H & F—Broadway (26)	HF1	−0.270	0.619**	−0.308	0.292	−0.135	−0.473*	0.209	0.232	−0.123	0.215
H & F—Brook Green (11)	HF2	−0.114	0.200	−0.018	0.200	−0.068	−0.178	0.057	0.296	−0.538	0.219
Richmond—Castelnau (16)	RI1	0.247	−0.147	0.171	−0.115	0.032	0.285	0.129	0.041	0.421	0.094
Wandsworth—High Street (11)	WA4	−0.187	0.578*	0.037	0.235	−0.204	0.147	0.534*	0.266	−0.099	0.138

[a] Associations are Spearman rank order correlations. Samples were limited to filters collected from December 2004 to March 2006. The numbers of samples are shown in parentheses. ** and * indicate that the associations observed at a given site were significant at $P < 0.01$ and $P < 0.05$, respectively (using a two-tailed test).

Table C.6. Associations Between Measures of PM_{10} Oxidative Potential (OP^{AA}/m^3 or OP^{GSH}/m^3) and Concentrations (µg/m^3) of Copollutants and Temperature (°C) for Samples Collected from December 2004 to March 2006[a]

Site	Code	NO	NO_2	NO_x	CO	SO_2	O_3	PM_{10}	$PM_{2.5}$	Temperature
OP^{AA}/m^3										
Bloomsbury—Russell Square	BL0	0.138 (14)	0.147 (14)	0.144 (14)	0.415 (14)	0.428 (14)	−0.281 (14)	0.780** (14)	0.837** (14)	0.009 (14)
Westminster—Marylebone Road	MY1	0.566** (55)	0.589** (55)	0.601** (55)	0.604** (55)	0.410** (55)	−0.535** (55)	0.842** (55)	0.840** (55)	0.338* (55)
Camden—Swiss Cottage	CD1	0.299 (16)	0.324 (16)	0.382 (16)	—	—	—	0.817** (16)	—	0.083 (17)
Haringey—Town Hall	HG1	−0.150 (12)	−0.028 (12)	0.539 (12)	—	−0.031 (12)	—	0.617* (12)	—	0.49 (12)
K & C—North Kensington	KC1	0.422 (13)	0.478 (13)	0.541 (13)	0.134 (13)	0.825** (13)	−0.305 (13)	0.886** (13)	—	−0.169 (13)
Greenwich—Eltham	GR4	0.048 (6)	0.021 (6)	−0.086 (6)	—	0.484 (6)	−0.232 (6)	0.829* (6)	—	0.393 (6)
Brent—Kingsbury	BT1	0.541 (8)	0.597 (8)	0.627 (8)	0.351 (7)	0.678 (8)	−0.482 (8)	0.541 (8)	—	−0.148 (8)
Camden—Shaftesbury Avenue	CD3	0.271 (10)	0.268 (10)	0.231 (10)	—	—	—	0.574 (11)	—	0.070 (11)
K & C—Cromwell Road	KC2	0.052 (21)	0.122 (21)	0.291 (21)	0.067 (21)	0.661** (21)	—	0.791** (21)	—	0.374 (21)
Southwark—Elephant & Castle	SK1	0.182 (14)	0.223 (14)	0.363 (14)	0.104 (14)	0.643* (14)	0.119 (12)	0.672** (14)	—	0.089 (14)
Southwark—Old Kent Road	SK2	0.264 (23)	0.277 (23)	0.286 (23)	−0.031 (22)	0.211 (22)	—	0.682** (24)	—	0.045 (24)
Lewisham—New Cross	LW2	−0.599* (11)	−0.603* (11)	−0.451 (11)	—	−0.003 (12)	—	0.325 (12)	—	0.42 (12)
H & F—Broadway	HF1	0.285 (26)	0.301 (26)	0.321 (26)	—	0.277 (25)	—	0.748** (26)	—	0.193 (26)
H & F—Brook Green	HF2	−0.194 (11)	−0.172 (11)	−0.069 (11)	—	—	—	0.709* (11)	—	0.437 (11)
Richmond—Castelnau	RI1	0.113 (16)	0.122 (16)	0.128 (16)	—	—	—	0.519* (16)	—	0.178 (16)
Wandsworth—High Street	WA4	0.633* (11)	0.642* (11)	0.636* (11)	0.550 (11)	—	—	0.866** (11)	—	0.239 (11)
Wandsworth—High Street	WA4	0.072 (11)	0.053 (11)	0.019 (11)	−0.009 (11)	—	—	0.188 (11)	—	0.367 (11)

Table continues next page

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[a] Associations are Pearson correlation coefficients. Samples were limited to filters collected from December 2004 to March 2006. Numbers of samples are shown in parentheses. ** and * indicate that the associations observed at a given site were significant at $P < 0.01$ and $P < 0.05$, respectively (using a two-tailed test).

Table C.6 (*Continued*). Associations Between Measures of PM_{10} Oxidative Potential (OP^{AA}/m^3 or OP^{GSH}/m^3) and Concentrations (µg/m^3) of Copollutants and Temperature (°C) for Samples Collected from December 2004 to March 2006[a]

Site	Code	NO	NO_2	NO_x	CO	SO_2	O_3	PM_{10}	$PM_{2.5}$	Temperature
OP^{GSH}/m^3										
Bloomsbury—Russell Square	BL0	0.694** (14)	0.654* (14)	0.412 (14)	0.718** (14)	0.541* (14)	−0.842** (14)	0.196 (14)	0.568* (14)	−0.482 (14)
Westminster—Marylebone Road	MY1	0.757** (55)	0.787** (55)	0.803** (55)	0.708** (55)	0.513** (55)	−0.574** (55)	0.736** (55)	0.653** (55)	0.467** (55)
Camden—Swiss Cottage	CD1	−0.009 (16)	0.019 (16)	0.153 (16)	—	—	—	0.365 (16)	—	−0.130 (17)
Haringey—Town Hall	HG1	0.818** (12)	0.785** (12)	0.339 (12)	—	0.260 (12)	—	−0.048 (12)	—	−0.264 (12)
K & C—North Kensington	KC1	0.619* (13)	0.525 (13)	0.251 (13)	0.110 (13)	0.193 (13)	−0.329 (13)	0.192 (13)	—	−0.102 (13)
Greenwich—Eltham	GR4	0.499 (6)	0.472 (6)	0.323 (6)	—	−0.148 (6)	−0.565 (6)	0.251 (6)	—	0.140 (6)
Brent—Kingsbury	BT1	0.970** (8)	0.941** (8)	0.652 (8)	0.67 (7)	0.343 (8)	−0.784* (8)	0.104 (8)	—	−0.271 (8)
Camden—Shaftesbury Avenue	CD3	−0.339 (10)	−0.342 (10)	−0.338 (10)	—	—	—	−0.371 (11)	—	0.444 (11)
K & C—Cromwell Road	KC2	−0.028 (21)	−0.075 (21)	−0.191 (21)	−0.212 (21)	−0.320 (21)	—	0.236 (21)	—	0.497* (21)
Southwark—Elephant & Castle	SK1	0.798** (14)	0.816** (14)	0.821** (14)	0.846** (14)	0.158 (14)	−0.887** (12)	0.597* (14)	—	−0.638 (14)
Southwark—Old Kent Road	SK2	0.845** (23)	0.863** (23)	0.789** (23)	0.506* (22)	0.154 (22)	—	0.579** (24)	—	−0.578** (24)
Lewisham—New Cross	LW2	0.590 (11)	0.438 (11)	0.029 (11)	—	0.359 (12)	—	0.189 (12)	—	−0.137 (12)
H & F—Broadway	HF1	0.759** (26)	0.769 ** (26)	0.670** (26)	—	0.588** (25)	—	0.535** (25)	—	−0.233 (26)
H & F—Brook Green	HF2	0.910** (11)	0.834** (11)	0.424 (11)	—	—	—	0.467 (11)	—	−0.163 (11)
Richmond—Castelnau	RI1	0.586* (16)	0.540*(16)	0.312 (16)	—	—	—	0.185 (16)	—	−0.146 (16)
Wandsworth—High Street	WA4	0.072 (11)	0.053 (11)	0.019 (11)	−0.009 (11)	—	—	0.188 (11)	—	0.367 (11)

[a] Associations are Pearson correlation coefficients. Samples were limited to filters collected from December 2004 to March 2006. Numbers of samples are shown in parentheses. ** and * indicate that the associations observed at a given site were significant at $P < 0.01$ and $P < 0.05$, respectively (using a two-tailed test).

Table C.7. Details of Tests of PM_{10} Toxicity Model

Model Run	Model Run Description	Traffic Flow/Speed[a]	Vehicle Exhaust PM	Tire Wear	Brake Wear	Rural and Background Concentrations[b]
1	2005 Base case	2005	Yes	Yes	Yes	Yes
2	2005 No vehicle exhaust	2005	No	Yes	Yes	Yes
3	2005 No tire wear	2005	Yes	No	Yes	Yes
4	1 – 2 (Vehicle exhaust)	2005	Yes	No	No	No
5	1 – 3 (Tire wear)	2005	No	Yes	No	No
6	2005 No vehicle exhaust, tire wear, or brake wear	2005	No	No	No	Yes
7	1 – 6 – 4 – 5 (Brake wear)	2005	No	No	Yes	No

[a] For all model runs, traffic flow and speed were maintained at the 2005 level.

[b] Rural concentrations reflect PM levels outside of London and background concentrations reflect non-traffic PM levels in London.

Table C.8. Source Apportionment of Modeled Estimates of PM_{10} Emissions (tonnes/yr) in 2005

Model Run Description	Vehicle Exhaust	Tire Wear	Brake Wear	Tire Wear and Brake Wear	Cold Start
2005 Base case	1495	449	576	1025	134

APPENDIX D. Calculation of Emissions from Tire Wear and Brake Wear

Emissions of PM_{10} from tire and brake wear were calculated based on a method consistent with that described in COPERT III (see Ntziachristos and Boulter 2003). The calculations were based on the number of vehicles (divided into six vehicle categories), vehicle speed, and assumptions about the number of axles and vehicle loads.

TIRE WEAR

Emissions from tire wear are calculated from the equation

$$TE_{Tij} = N_j \times M_j \times f_{Ti} \times (EF_{T\ TSP})_j \times S_T(V),$$

where Nj = the number of vehicles in vehicle category j; Mj = mileage per vehicle (km); f_{Ti} = the fraction of TSP that can be classified as PM_{10} (0.6) or $PM_{2.5}$ (0.42); $(EF_{T\ TSP})_j$ = the TSP emission rate in mg/km at a speed of 80 km/hr for the vehicle category j (passenger car, light goods vehicle [LGV], heavy goods vehicle [HGV], or motorcycle); and $S_T(V)$ = the speed correction factor, which depends on the mean vehicle velocity (V).

For $V < 40$ km/hr, $S_T = 1.39$. For $V \geq 40$ km/hr and $V < 90$ km/hr, $S_T = -0.00974 \times V + 1.78$. Otherwise $S_T = 0.902$. The values used for $(EF_{T\ TSP})_j$ are 10.7 mg/km for passenger cars, 16.9 mg/km for LGVs, and 4.6 mg/km for motorcycles. Values for HGVs and buses are calculated by

$$(EF_{T\ TSP})_j = N_{axle} \times LCF \times (EF_{T\ TSP})_j / 2,$$

where N_{axle} = number of axles (i.e., assumed 2 for buses, 2.28 for "rigid" vehicles, and 5 for "articulated" vehicles), and LCF = load correction factor (assumed 50%).

BRAKE WEAR

Emissions from brake wear are calculated from the equation

$$TE_{Bij} = N_j \times M_j \times f_{Bi} \times (EF_{B\ TSP})_j \times S_B(V),$$

where Nj = the number of vehicles in vehicle category j; M_j = mileage per vehicle (km); f_{Bi} = the fraction of TSP that can be classified as PM_{10} (0.98) or $PM_{2.5}$ (0.39); $(EF_{B\ TSP})_j$ = the TSP emission rate in mg/km at a speed of 80 km/hr for vehicle category j; and $S_B(V)$ = the speed correction factor, which depends on the mean vehicle velocity (V).

For $V < 40$ km/hr, $S_B = 1.67$. For $V \geq 40$ km/hr and $V < 95$ km/hr, $S_B = -0.027 \times V + 2.75$. Otherwise $S_B = 0.185$. The values for $(EF_{B\ TSP})_j$ are 7.5 mg/km for passenger cars, 11.7 mg/km for LGVs, and 3.75 mg/km for motorcycles. Values for HGVs and buses are calculated by $(EF_{B\ TSP})_j = 3.13 \times LCF \times (EF_{B\ TSP})_j$, where LCF = load correction factor (assumed 50%).

APPENDIX E. Standardization of Oxidative Potential Measurements

The antioxidant depletion data referred to in this report were obtained from 33 separate batches of samples. It was therefore necessary to control for batch-to-batch variation in the initial starting concentrations of antioxidants and the auto-oxidative losses observed in the particle-free controls during the 4-hour incubation period.

Variation in starting concentrations of AA and UA in the particle-free controls, at time zero (C0) across each of the individual incubations were corrected by adjusting the individual batch concentration to the known starting concentration of 200 µM, such that the C0 correction factor = 200/batch C0. All the data in each batch's data set (concentrations at 0 and 4 hours) were then multiplied by this factor. A second factor was then derived to correct for the variation in background oxidation in the particle-free controls after the 4-hour incubation (C4). The average 4-hour concentration across all 33 batches was calculated after the C0 adjustment. This value was then divided by the individual batch's particle-free 4-hour concentrations, such that the C4 correction factor = mean C4 for all batches/batch C4. All the 4-hour data in each batch's data sets were then multiplied by this factor.

A similar approach was adopted for GSH. However because GSH was measured indirectly, that is, by the subtraction of the determined glutathione disulfide from the total glutathione concentration (i.e., GSx [GSH + 2 × GSSG]), batch-to-batch variations had to be controlled separately for both GSSG and GSx data sets, such that for each batch the GSx C0 correction factor = 200/batch C0, based on the known starting concentration of 200 µM. As for the AA and UA data sets, each batch (both GSx and GSSG) was multiplied by its respective C0 corrections factor. The concentration of GSSG measured in each batch at time 0 was subtracted from the respective GSSG data set, because the C0 value should be zero. The C4 factor for GSx was calculated for each batch as outlined for AA and UA, such that C4 correction factor = mean C4 for all batches/batch C4. The C4 correction factor for GSSG was determined by calculating the average 4-hour GSSG concentration across all 33 incubations and relating this to the depletions observed in each individual batch, such that the C4 correction factor = mean C4 for all batches − batch C4. This approach of subtracting an absolute molar value to correct for batch-to-batch variations for GSSG was employed because of the high degree of batch-to-batch variability in relation to the measured concentrations. The final GSH concentration was finally established using the formula GSH = GSx − (2 × GSSG) using the data from the standardized data sets.

ABOUT THE AUTHORS

Frank Kelly obtained his Ph.D. in 1982 and holds the chair in environmental health at King's College London where he is also head of the Environmental Research Group and deputy director of the MRC-HPA Centre for Environment & Health. He has considerable experience in managing and coordinating interdisciplinary research in multicenter projects, including the HEI-funded CCS study and the Low Emission Zone baseline study. He contributes to the activities of a number of expert groups including U.K. government and WHO panels.

Ross Anderson is professor of epidemiology at the Centre for Epidemiology at St. George's, University of London. He has an international reputation as a leading researcher in the field of air pollution epidemiology, having a long track record of national and international research commitments. He is a member of the Expert Panel on Air Quality Standards (EPAQS) and the WHO Air Quality Expert Group. He was also a member of the U.S. National Academy of Science committee that reported on methods for estimating the health benefits of reducing ambient air pollution through regulations.

Ben Armstrong is an applied medical statistician at the London School of Hygiene & Tropical Medicine, with longstanding interest in the application of statistics to environmental health. He is a member of the Committee on the Medical Effects of Air Pollution (COMEAP) and the HEI Health Review Committee.

Richard Atkinson is a lecturer in statistics at St. George's, University of London, and has a special interest in the methods for quantifying the health impacts of outdoor air pollution. He is member of the COMEAP sub-committee set up to reevaluate the evidence for health effects of outdoor air pollution.

Ben Barratt has worked within the Air Quality Monitoring Team at the Environmental Research Group, King's College London since 1994 and is currently deputy manager. His key skills lie in establishing and managing regional air quality monitoring networks and interpreting monitoring results through software systems development, internet reporting methods, and assessment intervention impacts.

Sean Beevers has more than 10 years of experience with air pollution measurement, and emissions and air pollution modeling at the Environmental Research Group, King's College London. He has managed the emissions assessments for a number of large infrastructure projects in London and South East England as well as a number of key London developments including the London Atmospheric Emissions Inventory and the Congestion Charging Impacts Assessment.

Dick Derwent is director at rdscientific. He has considerable experience working with large data sets, extensive understanding of air quality issues in London, and a background in atmospheric science. He is a member of AQEG, EPAQS, and the WHO Air Quality Expert Group.

David Green manages the 16 monitoring sites within the LAQN that are affiliated with the AURN. In 1995, the Environmental Research Group, King's College London, became the first Regional Management Unit of the (then) Automatic Urban Network. David managed the installation of the Marylebone Road site and is responsible for its operation. It is situated on the IRR (boundary of the CCZ) and gathers the most comprehensive set of air pollution data in the AURN. His research interests include methods for measuring airborne particles.

Ian Mudway leads the Lung Biology Group at King's College London and has 15 years of experience studying the oxidative basis of air pollution, initially focusing on the oxidative gases ozone and NO_2, but more recently addressing the toxicity of ambient and vehicle-derived particulates.

Paul Wilkinson is an environmental epidemiologist and public health physician at the London School of Hygiene & Tropical Medicine, with particular interest in environmental hazards to health, including climate change and outdoor air pollution. He is holder of a Public Health Career Scientist Award, which focuses on the methods of assessing quantitative public health impacts.

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ABBREVIATIONS AND OTHER TERMS

AA	ascorbate
ANOVA	analysis of variance
BCS	bathocuproine disulfonic acid
BPS	bathophenanthroline disulfonate
CAT	catalase
CB	carbon black
CCS	Congestion Charging Scheme
CCZ	congestion charge zone
CO	carbon monoxide
DES	desferroxamine mesylate
DMSO	dimethylsulfoxide
DTNB	5,5′-dithiobis-(2-nitrobenzoic acid)
DTPA	diethylenetriamine pentaacetic acid
EDTA	ethylenediamine tetraacetic acid
FDMS	Filter Dynamics Measurement System
Fe_2O_3	hematite
Fe_3O_4	magnetite
GSH	glutathione
GSSG	glutathione disulfide
GSx	total glutathione
HCl	hydrocloric acid
H_2O_2	hydrogen peroxide
HGVs	heavy goods vehicles
HPLC	high performance liquid chromatography
ICP–MS	inductively coupled plasma mass spectrometry
K_2HPO_4–H_3PO_4	potassium phosphate buffer
LGV	light goods vehicles
NADPH	nicotinamide adenine dinucleotide phosphate
NO	nitric oxide
NO_2	nitrogen dioxide
NO_x	nitrogen oxides
$O_2^{-\bullet}$	oxygen radical
O_3	ozone
OP	oxidative potential
PAH	polyaromatic hydrocarbon
PM	particulate matter
$PM_{0.1}$	particulate matter with an aerodynamic diameter ≤ 0.1 μm
PM_1	particulate matter with an aerodynamic diameter ≤ 1 μm
$PM_{2.5}$	particulate matter with an aerodynamic diameter ≤ 2.5 μm
PM_{10}	particulate matter with an aerodynamic diameter ≤ 10 μm
ROFA	residual oil fly ash
RTLF	respiratory tract lining fluid
SO_2	sulfur dioxide
SOD/CAT	mixture of superoxide dismutase and catalase
TEOM	tapered element oscillating microbalance
TNB	5-thio-2-nitrobenzoic acid
TSP	total suspended particles
UA	urate

CHEMICAL ELEMENTS

Al	aluminium
As	arsenic
Ba	barium
Be	beryllium
Ca	calcium
Cd	cadium
Cu	copper
Fe	iron
Mn	manganese
Mo	molybdenum
Ni	nickel
Pb	lead
Sb	antimony
V	vanadium
Zn	zinc

COMMENTARY

Health Review Committee

Research Report 155, *The Impact of the Congestion Charging Scheme on Air Quality in London,* F. Kelly et al.

INTRODUCTION

The study of the London Congestion Charging Scheme (CCS*) conducted by Professor Frank Kelly, of King's College London, U.K., and colleagues originated in response to Request for Applications 04-1, "Measuring the Health Impacts of Actions Taken To Improve Air Quality" (Health Effects Institute 2004), issued as part of HEI's outcomes research program (see the Preface for a summary of this program), was created to (1) fund studies to assess the health impact of regulatory and incentive-based actions at levels ranging from local to national in order to improve air quality and (2) develop the methods required for, and specifically suited to, conducting such research. Although the primary intent of the RFA was to fund research aimed at estimating the impact of actions taken in the United States, proposals for studies of actions taken in other countries were also considered if the studies were relevant to current U.S. conditions (e.g., studies of interventions designed to reduce emissions in circumstances where emission levels and sources were comparable to those found in North America). The RFA primarily sought studies of intentional interventions (rather than natural or unplanned experiments, such as the closing of a steel mill in Utah Valley, Utah [Pope 1989; Pope et al. 2007]).

In response to RFA 04-1, Kelly and a multidisciplinary team of coinvestigators at St. George's Hospital and the London School of Hygiene and Tropical Medicine submitted an application entitled "Congestion Charging Scheme in London: Assessing Its Impact on Air Quality and Health" in April 2004. The team proposed studying the effects of the CCS, a regulatory action implemented in London in February 2003 with the primary aim of reducing traffic congestion by charging fees for vehicles entering the central part of London. The investigators proposed a 2.5-year study to evaluate whether the anticipated reduction in traffic congestion would lead to improved air quality in inner London and whether this improvement would in turn lead to improved health outcomes.

The investigators initially proposed three main objectives: (1) the development of an analytic framework for assessing ambient air quality data to evaluate the impact of the CCS on air quality, (2) the development and use of a new assay to measure the oxidative activity of ambient particulate matter (PM) in order to evaluate the impact of the CCS on the toxicologic properties of ambient PM, and (3) an examination of emergency hospital admissions, mortality records, and health indicators at the primary-care level in order to evaluate the impact of the CCS on health outcomes.

Because the CCS was not specifically aimed at improving air quality, the HEI Health Research Committee recommended postponing the evaluation of health outcomes until the investigators had completed the assessment of actual changes in air quality associated with the CCS. The Committee also recommended that the investigators include an evaluation of a planned Western Extension of the congestion charging zone (CCZ) and measurement of additional pollutants. The investigators subsequently submitted a revised application that focused on the first two objectives of the original application. The revised application was evaluated by the Committee, which recommended the study for funding.

SCIENTIFIC BACKGROUND

Even when interventions are undertaken with the specific goal of improving air quality, measuring their potential health impact is challenging. If the intervention takes place gradually, the resulting changes in air pollution and health outcomes, if any, will also be gradual. Changes in health outcomes that accompany gradual changes in pollutant concentrations can also result from concurrent changes in social, economic, or other factors, making it difficult to disentangle the changes and to characterize the actual role of the air quality interventions.

Professor Kelly's 3-year study, "Congestion Charging Scheme in London: Assessing Its Impact on Air Quality and Health," began in January 2005. Total expenditures were $760,400. The draft Investigators' Report from Kelly and colleagues was received for review in July 2007. A revised report, received in June 2008, was further revised and submitted in February 2009; it was accepted for publication later that month. During the review process, the HEI Health Review Committee and the investigators had the opportunity to exchange comments and to clarify issues in both the Investigators' Report and the Review Committee's Commentary.

This document has not been reviewed by public or private party institutions, including those that support the Health Effects Institute; therefore, it may not reflect the views of these parties, and no endorsements by them should be inferred.

* A list of abbreviations and other terms appears at the end of each Investigators' Report.

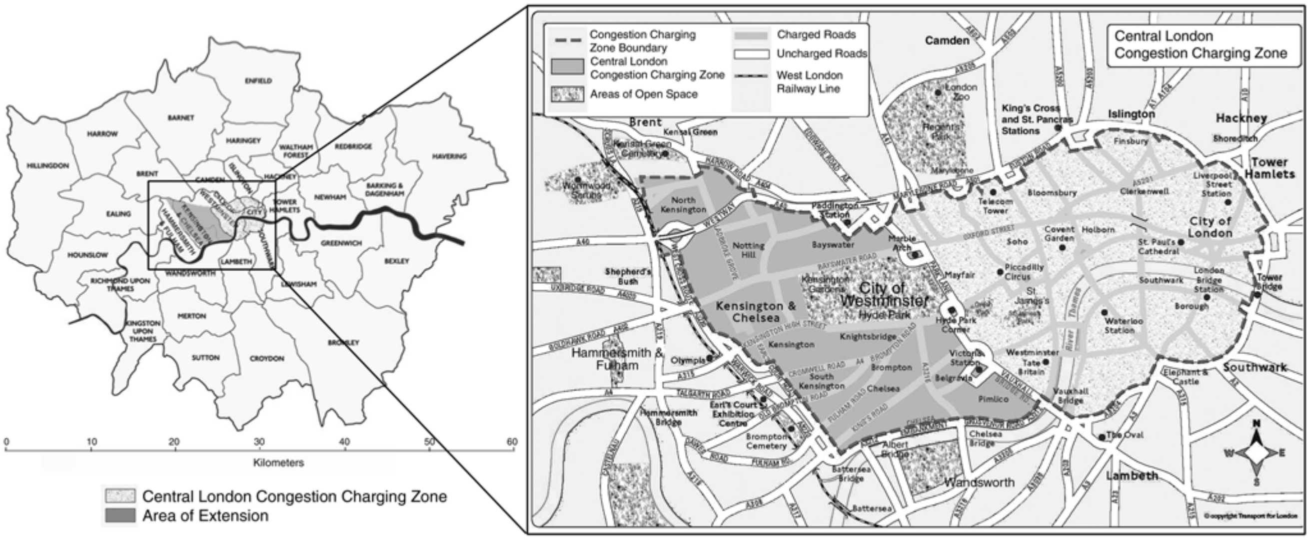
By contrast, studies that evaluate a discrete, stepwise change in pollution can be less complex and therefore more convincing. Some recent examples include studies of the impacts of a regulatory order forcing removal of sulfur from fuel oil in Hong Kong (Hedley et al. 2002), a ban on coal sales in Dublin, Ireland (Clancy et al. 2002), and the shutdown of a smelter by a strike in Utah (Pope et al. 2007).

Because changes in traffic regulations can also be implemented in a relatively short period of time, recent major interventions to reduce traffic congestion have attracted attention as opportunities to study the health impacts of changes in air quality that might accompany the changes in traffic congestion. When the London CCS study was launched, very few such studies had been undertaken. One of the first was a study by Friedman and colleagues (2001) of the impact on air quality of measures to reduce traffic during the 1996 Summer Olympic Games in Atlanta, Georgia. That study was subsequently reevaluated in an HEI-funded study (Peel et al. 2010). However, as these and the subsequent study by Kelly have shown, interventions whose primary goal was not improving air quality pose additional challenges to research on the impact of air quality changes on health outcomes.

LONDON CONGESTION CHARGING SCHEME

The London CCS was an appealing target for investigation because of the relatively discrete nature of the intervention. In February 2003, the city of London began charging a daily fee of 5 Great Britain pounds (about 8 U.S. dollars in 2003) to private vehicles entering the CCZ, an area of 22 km^2 that comprises some of the most congested areas of central London. The scheme encouraged alternative forms of transport (electric-powered vehicles, vehicles with nine or more passengers, and certain motorized tricycles) and increased the number and frequency of public buses. The hours of operation were 7:00 AM to 6:00 PM on weekdays. The fee was subsequently increased to GBP 8 in July 2005, and the zone was extended westward (the Western Extension) in February 2007 to include a total of 41.5 km^2, or approximately 2.6% of Greater London. Commentary Figure 1 shows a map of Greater London with the CCZ in the center; the original CCZ and the Western Extension are shown in the inset.

The primary objective of the CCS was to reduce traffic congestion (measured in vehicle kilometers traveled) in central London. However, the city's transportation agency, Transport for London (TfL), with the involvement of members of the investigators' team, had conducted feasibility studies for the design of the CCS that suggested that the intervention might also reduce emissions of nitrogen oxides (NO_x) and PM with an aerodynamic diameter ≤ 10 µm (PM_{10}) within the CCZ by about 12% each over the first year of the scheme (Beevers and Carslaw 2005). Once the scheme was in place, immediate impacts on traffic levels and speeds were observed in the first year of operation. TfL reported that traffic (number of vehicles with four or more



Commentary Figure 1. The London CCZ and Western Extension within Greater London.

wheels) entering the CCZ during charging hours had declined by 18% and that traffic speeds within the zone had increased by about 30% compared with pre-CCS levels (TfL 2004), although neither of these improvements were entirely sustained in subsequent years (TfL 2007). For the HEI study, Kelly and his team set out to determine whether the reductions in traffic during the first 2 years of CCS operation led to lower concentrations of selected air pollutants and to changes in the oxidative potential of PM_{10}.

The London CCS was also an attractive target of investigation because the city was one of the largest in recent years to undertake such an experiment and had already established an air quality monitoring network. These factors increased the likelihood of detecting changes in air quality. Larger programs have been put in place — Singapore, for example, has had a successful program to reduce traffic congestion in the central city since the 1970s. However, the Singapore program has not been studied for its impact on air quality or health. With traffic congestion and its impacts on air quality growing in major cities around the world, interest in interventions like the London CCS has been increasing. Stockholm, Sweden, for example, piloted a congestion charging program in 2006 (Eliasson 2008) that has since been made permanent. Similar interventions have been considered in other large cities in the United Kingdom and the United States.

OUTCOMES EVALUATION CYCLE

Studies can evaluate the influence of particular interventions at various points in the "Outcomes Evaluation Cycle" (described in the Preface to this report) that links an intervention stepwise to its hypothesized effects on human health (van Erp and Cohen 2009). The study that Kelly and colleagues conducted addressed three steps in this chain: regulatory or other action (providing evidence that the intervention or controls have been put in place); emissions (determining whether the intervention or controls have reduced emissions, whether emitters have changed their practices, and whether there have been unintended consequences); and ambient air quality (determining whether the intervention or controls have resulted in improved air quality).

Although the investigators were not funded to look at health outcomes, they essentially proposed an intermediate alternative, which was to characterize London's PM_{10} in terms of its potential to initiate oxidative stress in biologic systems. The ability of air pollutants to initiate oxidative stress is theorized to be a mechanism by which they exert adverse impacts on human health (Gilliland et al. 1999). Several studies have suggested that PM, diesel exhaust, or some of their components — such as transition metals (e.g., iron [Fe], copper [Cu], chromium [Cr], nickel [Ni], and vanadium [V]) and organic compounds (e.g., polycyclic aromatic hydrocarbons and quinones) — may play a role in inducing oxidative stress (Li et al. 1996, 2002, 2003; Nel et al. 2001; Xia et al. 2004). Because isolating the effects of individual components of the complex PM mixture is challenging, investigators have in recent years begun exploring methods that could provide an aggregate measure of PM's ability to cause oxidative stress.

The approach taken in this study was to measure the oxidative activity of extracts from PM filters from London in an in vitro, acellular assay (Zielinski et al. 1999; Mudway et al. 2004) and to derive quantitative metrics for oxidative potential. Kelly and colleagues then sought to examine how that potential might vary across London and how it might change following implementation of the CCS as a result of traffic-related impacts on the composition of ambient PM.

SUMMARY OF THE STUDY'S SPECIFIC AIMS

Kelly and his colleagues proposed the following specific aims for the study:

1. To update and verify the tools needed to construct detailed comparative emission scenarios; estimate the concentrations of pollutants for the CCZ and surrounding areas; and examine the possible impact of the CCS through detailed modeling.
2. To assemble an air pollution database of pollutant measurements from monitoring sites in Greater London to assess the impact of the CCS.
3. To examine a range of statistical and graphical approaches to analyzing the emissions and monitoring data.
4. To examine the oxidative potential of PM collected on archived filters from monitoring sites before and after the introduction of the CCS.

Research conducted to meet the first three specific aims is presented in Part 1 of this Research Report; and the research on the oxidative potential of PM is reported in Part 2. This Health Review Committee's Commentary initially follows the structure of the Investigators' Report, presenting the methods and findings separately for Parts 1 and 2 of the study. However, the Committee's evaluation of the research considers the entire project as well as its contributions to understanding the impact of the CCS on London's air quality and to developing methods for health outcomes research in general.

PART 1. EMISSIONS MODELING AND ANALYSIS OF AIR POLLUTION MEASUREMENTS (SPECIFIC AIMS 1–3)

METHODS

Modeling the Impacts of the CCS on Air Pollution (Specific Aim 1)

Modeling Emissions Kelly and colleagues refined and repeated earlier feasibility studies conducted for TfL to improve predictions of the potential impacts of the CCS on air quality within and outside the CCZ (Beevers and Carslaw 2005) and to help guide decisions about which air quality monitors would be used to evaluate changes in pollutant measurements. They began by using recent estimates of emissions from vehicular and non-vehicular sources throughout London from 2001 through 2004; that is, using emission estimates for the 2 years before (2001–2002; pre-CCS period) the scheme was introduced, and the 2 years after (2003–2004;post-CCS period). The earlier feasibility studies had been based on the London Atmospheric Emissions Inventory (LAEI) data published in 2002 whereas the analyses in this study were based on the LAEI 2003 emissions inventory (Mattai and Hutchinson 2006).

The investigators used the King's College London Emissions Toolkit, a linked set of databases and emission models, to develop scenarios of vehicular traffic emissions for the road network within and outside the CCZ (for details, see Appendix D to Part 1 of the Investigators' Report, available on the HEI Web site). This Emissions Toolkit was used to simulate vehicle emissions (g/km/sec) for specified road segments throughout Greater London, based on 24-hour traffic flows (vehicle kilometers traveled) and speeds (km/hr), each expressed in terms of annual average daily traffic. Total emissions for the modeled area were expressed in metric tonnes/year (a metric tonne is 1000 kg or ~ 2205 pounds). Projections of vehicle emissions were based on data and on assumptions about the mix of vehicle stock and the standard speed-related emission curves for various vehicle types for NO_x, nitrogen dioxide (NO_2), carbon monoxide (CO), PM_{10} from exhaust, and PM_{10} from tire and brake wear.

For this project, the investigators tailored and updated the emission models for the periods before and after introduction of the CCS in several ways. They adjusted the input assumptions about the age and types of vehicle stock to include stock specific to London (e.g., London Transport buses and taxis). Emissions were adjusted using assumptions to simulate the effects of exhaust after-treatment devices such as the fitting of particle traps or selective catalytic reduction systems in the London bus fleet. Comprehensive counts of traffic entering and leaving the charging zone across specific entry and exit points were conducted twice yearly by TfL (2004) and were used to estimate annual traffic volumes for each year of the study. Vehicle speed estimates were updated each year using average speed data from a continuously circulating vehicle in London.

Emissions from all non-vehicle sources (i.e., industrial processes; large boiler plants; domestic and commercial fuel combustion; agriculture; and air, rail, and ship transport) were also estimated using the 2003 London Atmospheric Emissions Inventory (Mattai and Hutchinson 2006). Emission estimates for NO_x, NO_2, and PM_{10} from this inventory were used in the HEI study.

Modeling Air Pollution Dispersion The investigators used the emission estimates as inputs to a set of databases, algorithms, and dispersion models, collectively referred to as the King's College London Air Pollution Toolkit. The Toolkit was used to predict ambient NO_x, NO_2, PM_{10}, and CO concentrations throughout London (for details of the Toolkit as applied to this study, see Appendix E to Part 1 of the Investigators' Report, available on the HEI Web site). Meteorologic data (temperature, wind speed and direction, relative humidity, and cloud cover) were obtained from the U.K. Meteorological Offices at Heathrow Airport for all years modeled. The models were first calibrated to reflect air pollution measurements at about 30 monitoring sites throughout London. Their performance was then compared with measurements at an additional 20 to 30 sites.

Total and source-specific concentrations were projected for London for the years 2001 through 2004 at a grid resolution of 20 by 20 m. Annual means for the entire study area (i.e., the mean of the concentrations for all 20-m^2 blocks) were also estimated for each pollutant and each year.

Statistical Methods and Data Analysis The investigators conducted a number of analyses to characterize the basic findings from the models. These analyses included mapping the spatial distribution of each pollutant concentration across the study area, and mapping the differences between projected concentrations for the years before and after the implementation of the CCS.

They also conducted sensitivity analyses to understand better the potential contributions of different sources and traffic scenarios to estimated pollutant concentrations. The first set of sensitivity analyses was designed to examine the relative contributions of rural, London background, and local roadside pollutant levels to predicted concentrations of NO_x, NO_2, and PM_{10}. (The London background contribution was calculated as the total contributions from all three sources minus the rural and local roadside contributions). The second set of sensitivity analyses examined the impacts of various scenarios involving changes in the flow (vehicle kilometers traveled) and speed (kilometers/hour) of key vehicle types (bus, taxi, and car) on pollutant concentrations within the CCZ and at the CCZ boundary. Results were expressed as a "slice" across the CCZ, a north–south transect with predictions at 20-m intervals, to show the variation in contributions to total pollutant concentrations in relationship to roadways.

Establishment of the CCS Study Database of Air Quality Measurements (Specific Aim 2)

The investigators established the CCS Study Database of air monitoring results with which to evaluate the actual changes in air quality associated with implementation of the CCS. The data were obtained from a subset of all fixed, continuous air monitoring sites that make up the three monitoring networks that feed into the London Air Quality Network (LAQN) database. The investigators sought to include sites that were representative of several broad classes of monitoring locations: rural, suburban or urban background (referred to generally as background), roadside, and curbside.

Data from all background and roadside monitoring sites in Greater London with a capture rate of at least 75% (that is, 75% of all days in the 4-year study period and on those days, 75% of valid hourly mean concentrations) were transferred from the LAQN database to the CCS Study Database. For locations within or on the boundary of the CCZ, data from all sites were included regardless of capture rate. Of the 102 sites, 32 were selected as "key indicator" sites for the detailed investigation of the impact of the CCS; these included all long-term continuous monitoring sites within and surrounding the CCS as well as a sample of control sites from areas in Outer London.

The final CCS Study Database consisted of fully validated (or ratified) 15-minute mean concentrations for CO, nitrogen oxide (NO), NO_2, NO_x, PM_{10}, $PM_{2.5}$, and black smoke from the 102 selected sites from February 17, 2001, through February 16, 2005, the 2 years before and after introduction of the CCS. However, the specific pollutants measured, the methods used to monitor the air, and the capture rates varied by site. For example, PM_{10} measurements were available for all key indicator sites during the period of the study, but $PM_{2.5}$ measurements were available for only three sites. Summary statistics based on hourly mean concentrations were compiled and daily mean time-series charts were created for each pollutant.

Analysis of Changes in Geometric Mean Pollutant Concentrations Measured Across London (Specific Aim 3)

The Investigators' Report placed primary emphasis on comparisons of temporal and spatial changes in the geometric mean concentrations of each pollutant at individual sites and across London. These analyses were based on data from the original CCZ and did not include data on the later Western Extension of the zone. Three hypotheses helped guide their analytic approach:

1. Any effects of the CCS would most likely be observed in pollutants whose main source in London was vehicles (i.e., NO, NO_2, NO_x, PM_{10}, and CO).
2. The effects of the CCS on air pollutant concentrations would be observed most readily during the hours the scheme was in operation — that is, during the day on weekdays (the "congestion charging hours").
3. The CCS would not have an effect on pollutant concentrations measured at sites 8 km or more from the CCZ center.

The locations of sites used to collect data for the CCS Study Database were grouped into three areas: within the CCZ not including its boundary, surrounding the CCZ up to 8 km from the center of the zone (roughly equivalent to Inner London), and more than 8 km from the center of the zone as a control area (roughly equivalent to Outer London; see Figure 16 in Part 1 of the Investigators' Report). Sites in the control area were assumed to be beyond the influence of the CCS and therefore indicative of regional trends in air pollution levels. All available monitoring sites within the CCZ were utilized in the analysis (one roadside site and three background sites).

The investigators paired each of the monitors in the zone with several monitors in Outer London and abstracted daily concentration data for only those days on which both of the paired monitors had data for a particular pollutant. For example, the Bloomsbury—Russell Square site, an urban background site within the CCZ, was paired individually with each of five urban background monitors in Outer London that also had data for PM_{10}. The number of Outer London sites available to be paired with a site within the CCZ differed by pollutant, as did the number of days with available data.

For each monitoring site within and outside the CCZ, the investigators first estimated the ratio of the post-CCS geometric mean to the pre-CCS geometric mean for each pollutant. They used a simple logistic regression model in which the natural log of the daily pollutant concentration was regressed on a dichotomous variable (pre-CCS [0] and post-CCS [1]) and the coefficient of the model was interpreted as an estimate of mean ratio of the post-CCS geometric mean concentration to the pre-CCS concentration.

Next, the investigators adjusted the ratios for pollutant concentrations at monitors within the CCZ for regional changes in air quality by calculating a "controlled ratio" of post/pre changes within the zone compared with post/pre changes in the control area. For each pair of monitors, the controlled ratio was calculated by taking the ratio of the post-CCS/pre-CCS geometric mean ratio at the monitor within the zone to the post-CCS/pre-CCS geometric mean ratio at the monitor in the control area (i.e., a ratio of post/pre ratios). For example, the Bloomsbury—Russell Square site was paired with five control sites, so a set of five controlled ratios was estimated. Each set of controlled ratios was combined into an overall mean ratio using random-effects meta-analysis methods (DerSimonian and Laird 1986).

The controlled ratios were stratified by weekday (including only the congestion charging hours) and by weekends (including matching hours). Weekday data were further stratified by location of site (roadside or urban background). Weekend data were analyzed only for background sites because limited data were available for roadside sites during the period of study.

A supplementary analysis was carried out that compared changes in geometric mean concentrations according to distance from the zone center. This supplementary analysis used measurements from 21 additional sites in the area surrounding the CCZ (from the CCZ boundary out to 8 km from the center of the zone; roughly equivalent to Inner London). That analysis has been more fully reported in a recent publication by Atkinson and colleagues (2009).

Additional Exploratory Analyses

The investigators explored three other analytic techniques for characterizing and evaluating the changes in NO, NO_2, NO_x, PM_{10}, and CO concentrations over the period of the study:

- use of ethane as a dispersion indicator;
- use of the cumulative sum (CUSUM) statistical technique to detect step changes in air pollution; and
- use of bivariate polar plots to characterize local emissions.

The investigators used ethane, an indicator of natural-gas leakage, to account for variability in air pollutant concentrations that might be attributable to broad-scale meteorologic conditions and thus to better isolate the impact of the CCS. They explored use of the CUSUM technique, a sequential analytic method for detecting statistically significant step changes in a parameter or distribution, to identify possible short-term changes in pollutant concentrations associated with the introduction of the CCS. The third approach, bivariate polar plot analysis, was used to provide a graphical representation of the effect of wind speed and direction on air pollutant concentrations at the Camden—Shaftesbury Avenue site, the sole roadside monitoring site within the CCZ. The investigators thought bivariate polar plot analysis might be used to identify potential local emission sources and thus help with the positioning of roadside monitoring sites. Ultimately, the HEI Review Committee and the investigators decided that, although these three methods showed potential value, they needed further investigation; they are therefore discussed only briefly in Part 1 of the Investigators' Report; fuller descriptions are given in several appendices available on the HEI Web site.

SUMMARY OF MAIN RESULTS FOR PART 1

Modeling Studies

The modeling studies predicted modest changes in NO_x, NO_2, and PM_{10} emissions (tonnes/year) and concentrations (ppb for NO_x and NO_2, and μg/m^3 for PM_{10}) across Greater London over the 4-year period of the study. Commentary Table 1 compares the projected average emissions and concentrations for the 2 years before and the 2 years after the CCS was introduced along with the change (and percent change) between the two time periods. Most of the emission reductions were accounted for by expected reductions within the zone. The models suggested about 20% reductions in NO_x and PM_{10} emissions in the zone for the 2 years following introduction of the CCS — greater reductions than the 12% predicted in the initial feasibility studies that preceded the CCS. However, the earlier estimates were based on a comparison of 2002 to 2003 only (Beevers and Carslaw 2005) and the investigators had reported that unusual meteorologic conditions had led to periods of elevated pollution levels in 2003.

Despite the somewhat larger modeled reductions in emissions, the average projected changes in concentrations of NO_x, NO_2 and PM_{10} related to the CCS were small (see Commentary Table 1). The investigators projected a net decrease of 1.7 ppb in the annual mean NO_x concentration within the zone (the net difference between a projected annual mean 3.6 ppb decrease within the zone and an annual mean 1.9 ppb decrease outside the zone). The projected net decrease of 0.8 μg/m^3 in the concentration of PM_{10} resulted from a projected average decrease of 0.4 μg/m^3 within the CCZ and an overall average increase of 0.4 μg/m^3 in projected PM_{10} concentrations in Greater London. The concentration of NO_2 was projected to increase slightly (0.1 ppb) in the zone due to the introduction of the CCS. However, this increase was projected despite an estimated mean decrease of 0.2 ppb across

Commentary Table 1. Comparison of Modeled Changes in Emissions and Concentrations of NO_x, NO_2, and PM_{10} After Introduction of the CCS[a]

	NO_x			NO_2			PM_{10}		
	Before CCS	After CCS	Difference (% Change)	Before CCS	After CCS	Difference (% Change)	Before CCS	After CCS	Difference (% Change)
Modeled Emissions (tonnes/year)[b]									
Within CCZ	1,409	1,132	−277 (−19.7)	206	197	−9 (−4.6)	120	95	−26 (−21)
Greater London—total	54,824	44,541	−10,283 (−18.8)	6,784	6,456	−328 (−4.8)	3,473	2,965	−508 (−14.6)
Modeled Average Concentrations (±SD)[c]									
Within CCZ	64.3 (30.6)	60.7 (27.2)	−3.6 (−5.6)	29.2 (7.1)	29.3 (7.3)	0.1 (0.3)	29.4 (6.3)	29.0 (5.4)	−0.4 (−1.4)
Greater London	35.5 (14.4)	33.6 (13.2)	−1.9 (−5.4)	20.1 (4.0)	19.9 (4.1)	−0.2 (−1.0)	23.9 (2.4)	24.2 (2.1)	0.4 (1.3)
Net change within CCZ[d]			−1.7 (−2.6)			0.3 (1.0)			−0.8 (−2.7)

[a] Modeled projections used the King's College London Air Pollution Toolkit and the LAEI 2003 data.

[b] Emission data (from Investigators' Report Part 1 Tables 2 [NO_x and NO_2] and 3 [PM_{10}]) were averaged for the 2 years before and the 2 years after the CCS was introduced in order to be comparable to the modeled average concentrations for these periods.

[c] NO_x, NO_2 in ppb; PM_{10} in µg/m³. Modeled concentration data are taken from Investigators' Report Part 1 Table 4.

[d] Net change within CCZ = change within CCZ minus change in Greater London.

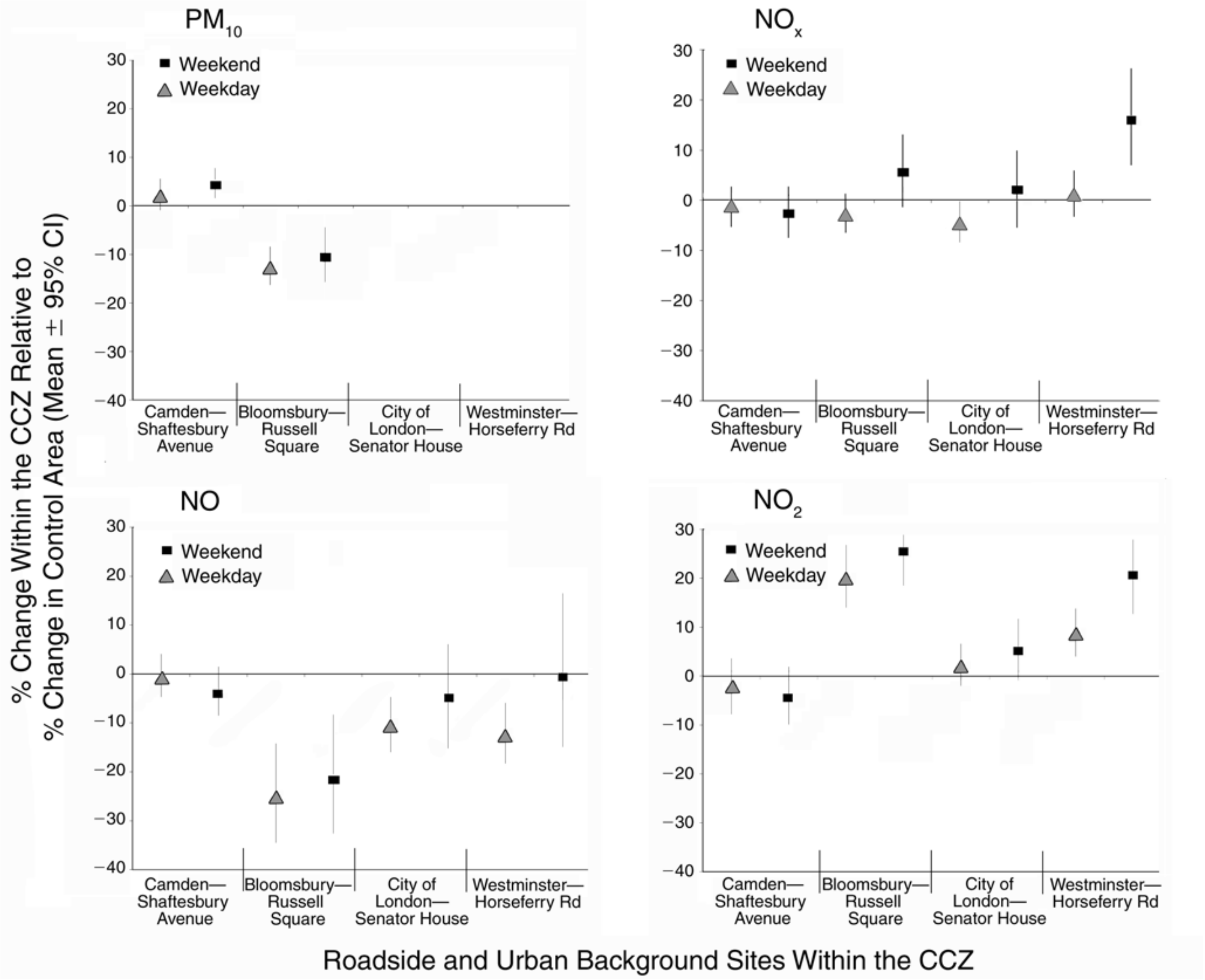
London due to vehicle fleet changes. Thus, the net effect was a projected increase of 0.3 ppb NO_2 within the zone. No results were provided for NO.

The investigators' analyses of the model's sensitivity provided insights into the difficulties the CCS study would face in using a limited number of monitoring sites to detect local and area-wide changes in air quality. Their first set of sensitivity analyses, which estimated potential source contributions to concentrations of NO_x, NO_2, and PM_{10} across a "slice" of the CCZ, predicted that the contributions from road traffic would strongly depend on the site and the road and therefore highlighted the limitations of relying on data from just one roadside site within the zone to assess the impact of the CCS (see, for example, results for PM_{10} in Figure 13 in Part 1 of the Investigators' Report). These analyses also provided an indication of the relative importance of broad-scale urban and regional background source contributions to overall PM_{10} concentrations, which further complicates efforts to detect the impact of the CCS. The transect analyses of NO_x concentrations across the zone showed similar patterns of road-related peaks, but source contributions from London and regional background to NO_x concentrations were not as dominant as those for PM_{10}. As a result of these findings, data from three background monitoring sites were later added to the CCS Study Database.

The investigators suggested that results from the second set of sensitivity analyses, which were designed to model the impact on air pollutants of CCS-related changes in vehicle speed and type observed by TfL, offered another possible explanation for the small net change in pollutant concentrations predicted by — and ultimately observed in — the monitoring data. Their results for PM_{10}, for example (shown in Figure 15 in Part 1 of the Investigators' Report), suggest that decreases in PM_{10} concentrations associated with reductions in car traffic and commensurate improvements in flow and speed may be at least partially offset by increases in PM_{10} concentrations associated with increases in bus and taxi traffic.

Analysis of CCS-Related Changes in Geometric Mean Pollutant Concentrations Measured Across London

The investigators concluded that CCS-related changes estimated from monitoring data for PM_{10}, NO_x, NO, and NO_2 concentrations were broadly consistent with the projections of a small effect from the CCS in the modeling studies. In the process of reaching their conclusion, the investigators primarily relied on their controlled ratio analyses but also considered results from their analyses of unadjusted data. These latter results, which have been explored more fully



Commentary Figure 2. Overview of the mean controlled ratios for PM$_{10}$, NO$_X$, NO, and NO$_2$ concentrations at roadside and urban background sites within the CCZ during weekday and weekend hours. Each point is the mean percent change (± 95% CI) in the geometric mean concentration of a pollutant at a monitoring site within the CCZ between the 2 years before and 2 years after the CCS was introduced compared with the same temporal changes observed at monitoring sites in the control area (based on data from Table 25 in Part 1 of the Investigators' Report). Controlled ratios were developed to account for temporal and spatial changes in pollutant levels that might have occurred in the Greater London area (see Table 21 in Part 1 and related text). The Camden—Shaftesbury Avenue site is at roadside; all others are background sites.

in published work (Atkinson et al. 2009) are not discussed in detail here.

Commentary Figure 2 shows the complete set of controlled ratios for the analysis, including all pollutants and sites, for both weekdays and weekends. Each panel of the figure presents the mean controlled ratio, expressed as a mean percent change in concentrations with 95% confidence intervals (95% CIs) calculated for each roadside and urban background site located within the CCZ relative to sites in the control area.

From their analysis of data from the one roadside site within the zone (Camden—Shaftesbury Avenue), the investigators concluded that implementation of the CCS had not resulted in a statistically significant change in roadside concentrations of NO$_X$ (−0.9%), NO (−0.4%), or NO$_2$ (−2.2%) during weekdays. They did conclude, however, that PM$_{10}$ concentrations appeared to increase on average by 2.3% at that site (Commentary Figure 2).

The investigators observed different patterns, however, in controlled ratios of concentrations measured at urban background sites in the CCZ during weekday charging hours (Commentary Figure 2). PM$_{10}$ concentrations declined by 12% relative to control sites at the one urban background site, Bloomsbury—Russell Square, within the CCZ. The investigators interpreted the relative decreases in NO at the three urban background sites as suggestive of a marginal impact of the CCS. The study results suggested that the background concentrations of NO_2 had increased slightly within the CCZ at the three background sites relative to control sites. The investigators interpreted these increases as consistent with the results of the modeling studies, in which they had projected that NO_2 would increase slightly, partly due to increases in primary NO_2 emissions resulting from the introduction of particle traps on diesel buses. Changes in NO and NO_2 changes largely offset one another resulting in generally small net changes in NO_x.

One of the study hypotheses was that the effects of the CCS would be most evident during the hours in which the scheme was in operation. However, from their comparison of weekday to weekend changes at background monitoring sites in the CCZ, the investigators concluded that there was no strong evidence of a unique weekday effect (Commentary Figure 2). The patterns of changes in the concentrations of PM_{10}, NO_x, NO, and NO_2 during the weekends were similar to those during the weekday hours of operation, even though weekend air quality appeared to differ in a small, but consistent way. One explanation the investigators gave for this result was that TfL's preliminary traffic data showed reduced traffic volume on weekends after implementation of the scheme.

The exploratory analyses using ethane as a dispersion indicator, the CUSUM technique to identify the approximate timing of changes in air quality related to the CCS, and bivariate polar plots to explore the impact of prevailing weather conditions on positioning of monitoring sites were considered by the investigators to be supportive of the main findings. They considered them to be potentially useful techniques for air pollution research, but ones still in need of further research.

INVESTIGATORS' CONCLUSIONS FOR PART 1

Overall, the investigators felt that their primary and exploratory analyses collectively suggested that the introduction of the CCS in 2003 was associated with small temporal changes in air pollutant concentrations compared with those in areas in Outer London. However, they concluded that a number of limitations precluded them from attributing these changes to the CCS alone. Among other factors, they pointed out that PM_{10}, NO_2, and O_3 concentrations were higher in 2003 than in 2002 because of unusual meteorologic conditions. They also acknowledged that the area covered by the CCS — approximately 1.4% of Greater London — was likely too small to be able to influence air pollutant concentrations significantly either within or outside the zone. They recommended that their experience with the modeling and measurement approaches used in this study be used to inform the design of studies and monitoring networks to assess the impact of future interventions, including the planned expansion of the CCZ (the Western Extension in 2007) and introduction of the larger Low Emission Zone (LEZ) project planned for London in 2008.

PART 2. ANALYSIS OF THE OXIDATIVE POTENTIAL OF PM_{10} (SPECIFIC AIM 4)

The primary objective of Part 2 of the study was to explore whether implementation of the CCS led to detectable changes in the oxidative potential or in the composition of the PM_{10} mixture. The secondary objective was to establish a more comprehensive baseline of monitoring data for use in future studies of the CCS by adding data from additional monitoring sites located within and outside the proposed Western Extension of the CCZ.

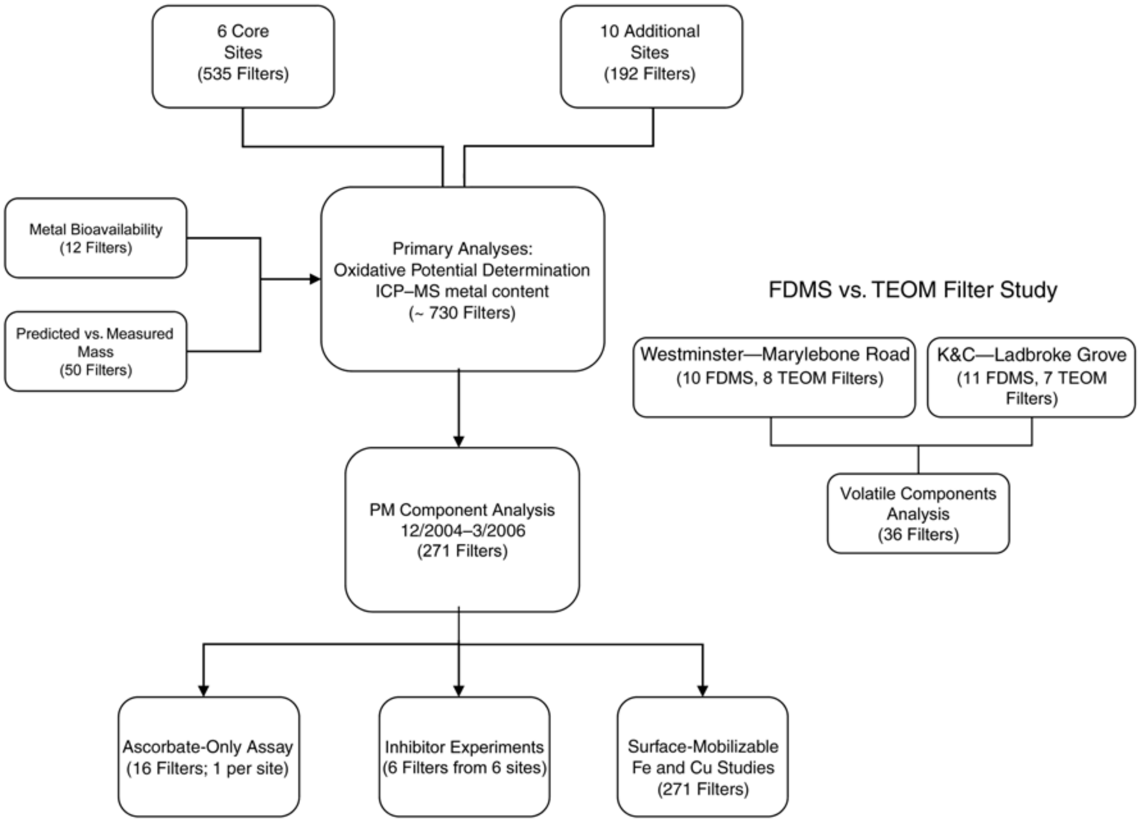
METHODS

The investigators conducted a number of primary and supplementary experimental analyses to develop and optimize the oxidative potential assays used to meet the objectives for Part 2 of the project. Commentary Figure 3 provides an overview of the analyses conducted and shows the site types and numbers of filters included in each one.

Filter Archive

The investigators created an archive of PM_{10} filters from tapered element oscillating microbalances (TEOMs) at 16 monitoring sites in the CCZ and in the surrounding area. These included filters from the six sites (one roadside and five background sites) in and adjacent to the original CCZ, collected over the period 3 years before and 3 years after the introduction of the CCS in February 2003. Filters collected from 2004 to early 2005 were added to the filter archive from 10 more TEOM monitoring sites located in and around the proposed Western Extension to the CCZ with the goal of creating a more complete database with which to study the impact of the larger CCS once the proposed Western Extension came into effect in February 2007 (see Table 1 in Part 2 of the Investigators' Report). A total of approximately 730 TEOM filters were obtained from the 16 sites and stored at King's College London at room temperature until extraction.

The investigators also collected a smaller number of filters from Filter Dynamics Measurement System (FDMS) monitors co-located along with TEOM monitors at two sites (one in and one outside the CCZ) to explore the impact of sampling method on the possible contributions to oxidative



Commentary Figure 3. Overview of experiments to investigate the oxidative potential of PM_{10}.

potential from volatile components of PM. Filters from the more commonly used TEOM monitors are collected at a higher temperature (50°C) than are FDMS filters (30°C for the base filter and 4°C for the purge filter). There is some concern that the higher TEOM sampling temperature drives off many of the volatile components of PM. The investigators also wanted to compare the two monitoring systems because the city of London is gradually replacing the TEOM monitors with FDMS monitors. FDMS filters were transferred into chilled methanol on site before being transported to King's College London where they were stored at −20°C until extraction.

Filter Extraction and Analysis

PM was extracted from the TEOM and FDMS filters using a standardized procedure, resuspended to a standard concentration in an aqueous solution containing 5% methanol (pretreated to remove any metal contaminants), and stored at −80°C until needed for analysis. Before these extractions, the investigators experimented with different ligand solutions to optimize the aqueous extraction of metals from the PM. Particle mass on the filters was represented by the mass reported from the TEOM monitors.

The investigators then measured the oxidative activity of the extracts using an acellular assay, which had been developed by Zielinski and colleagues (1999) and further used by Mudway and colleagues (2004, 2005) to study several types of particulates. The basic assay measures the capacity of the extracts to deplete antioxidants in a synthetic respiratory tract lining fluid (RTLF) within a fixed time period. The synthetic RTLF is made up of equimolar concentrations of ascorbate, urate, and reduced glutathione, three common antioxidant compounds found in fluids on the surface of the lining of the lung; no lung tissue or cells were present in the RTLF. The reduction in the concentration of each antioxidant after addition of a standard aliquot of extract was hypothesized to reflect the raw oxidant activity of the PM from which it was derived. Positive (residual oil fly ash [ROFA]), negative (carbon black), and particle-free controls were run in parallel with each batch of samples. All incubations with the synthetic RTLF were performed in triplicate. Each filter extract was also assayed for a panel of metals previously associated in published studies with traffic sources: aluminum (Al), arsenic (As), barium (Ba), beryllium (Be), cadmium (Cd), Cu, Fe, manganese (Mn), molybdenum (Mo), Ni, lead (Pb), V, and zinc (Zn) (see

Table 2 in Part 2 of the Investigators' Report). Their concentrations were determined using inductively coupled plasma mass spectrometry (ICP–MS). Each batch of samples was run with an aqueous extract of ROFA as a positive control and an ultrapure-water blank.

Derivation of Metrics for Oxidative Potential

Kelly and colleagues first evaluated whether the synthetic RTLF model was a good potential indicator of oxidative activity in PM_{10}. They found that the extracts from the 730 filters demonstrated considerable variability in their capacity to deplete ascorbate and glutathione but not urate (which may be explained by other studies showing that it is a preferential scavenger of gaseous pollutants such as ozone and NO_2; Mudway and Kelly 1998). Consequently, further comparisons of oxidative activity were based only on glutathione and ascorbate results.

The investigators defined "oxidative potential" as the percentage of loss of either ascorbate or of glutathione relative to the particle-free control in the synthetic RTLF assay. Oxidative potential for ascorbate was abbreviated as OP^{AA} and for glutathione as OP^{GSH}. Two metrics for oxidative potential were developed. The first was expressed as the percent depletion of each antioxidant per unit of mass of PM_{10} (OP/µg PM_{10}) and provided a common basis for comparing the amount of metals and other PM constituents in samples. In the second, oxidative potential was expressed per unit volume of air sampled (OP/m^3) and provided a more direct measure of the oxidative potential of the ambient PM concentrations at the different monitoring sites. No correlation was found between OP^{AA}/µg and OP^{GSH}/µg, which the investigators suggested was an indication that the two antioxidants were sensitive to different oxidants (and perhaps PM sources).

Characterization of Contributors to Oxidative Potential

Following their initial analysis of all the samples, the investigators conducted several supplemental experimental studies to help identify the key chemicals that might be responsible for the oxidative potential measured:

- Ascorbate-only assay. In order to determine the overall fraction of oxidative potential that might be attributable to metals, the investigators used an assay in which ascorbate was the only antioxidant present in the synthetic RTLF. Extracts representative of the mean oxidative potential detected at 16 sites were analyzed with and without the chelating agent, diethylene triamine pentaacetic acid (DTPA), to bind up any transition metals present in the extracts
- Inhibitor experiments. Using six filter samples chosen to represent low and high oxidative potential (per µg PM_{10}) based on glutathione depletion, ascorbate depletion, or both, the investigators incubated the filter extracts with specific inhibitors and metal chelators to explore the possible contributions of secondary superoxides, hydroxyl radicals, and transition metals onto the levels of oxidative activity observed.
- Surface-mobilizable Fe and Cu studies. The investigators also conducted experiments to obtain a more informative estimate of bioavailable Fe and Cu. They measured the separate contributions of total surface-mobilizable Fe (Fe^{2+} and Fe^{3+}) and Cu (Cu^{+} and Cu^{2+}) concentrations by incubating extracts with chromogenic chelators specific to Fe or Cu, bathophenathroline disulfonate and bathocuproine disulfonic acid, respectively. These chelators have affinities for Fe and Cu similar to many of the major biological ligands in vivo.

The comparison of oxidative potential of filter extracts from co-located TEOM and FDMS monitoring sites was used to indicate the extent to which oxidatively active volatile species, including ammonium nitrate and organic species, might have been driven off by the higher sampling temperature of the TEOM monitor.

Finally, the investigators conducted a set of analyses designed to assess the relative contributions of motor vehicle exhaust, tire wear, and brake wear to PM_{10} concentrations and oxidative potential measured at the 16 sites. They first used emissions and dispersion models to develop estimates of primary PM_{10} as a function of relative contributions of motor vehicle exhaust, tire wear, and brake wear and checked them for consistency with measured primary PM_{10} (total measured PM_{10} minus a contribution of rural background PM_{10}). They then examined correlations between these modeled contributions (of motor vehicle exhaust, tire wear, and brake wear) to the various measures of oxidative potential determined for each site.

Data Analysis

The investigators conducted four sets of analyses.

1. They first used the whole data set — about 730 filter samples from all sites over the full duration of the study. Their statistical analysis of this data set began with descriptive analyses of all the variables (PM_{10}, copollutants [NO_x, NO, NO_2, CO, SO_2, and O_3], metals, and oxidative potential metrics) using all of the data available from the monitors. The investigators then explored the correlations between PM metal concentrations, the various measures of oxidative potential, and copollutant concentrations. Correlations between normally distributed variables were assessed using Pearson correlation coefficients. Where one or both of the parameters under consideration were non-normally

distributed, the Spearman rank-order test of correlation was used. They first used stepwise multiple linear regression with a backward deletion approach to model the associations between PM_{10} metals or copollutants and oxidative potential. However, in response to the Health Review Committee's concerns about the impact of clustering of data by site and by temporal autocorrelation in the data, the investigators conducted alternative analyses using more robust statistical techniques (regressions carried out with Huber–White sandwich estimators of standard error and use of generalized estimating equations to reflect correlation between sites and over time).

2. They next analyzed data from the original six sites selected to evaluate the impact of the CCS on the oxidative potential and composition of PM_{10} over time and by monitor location (roadside versus urban background).
3. The investigators next examined the spatial variability in PM oxidative potential and composition using the original six sites and the ten sites added to support evaluation of the Western Extension. Oxidative potential and composition data were summarized by monitoring site and by site type (urban background, curbside, or roadside). The oxidative potentials of filter extracts from the TEOM and FDMS filters from co-located monitors were also compared. For the second and third sets of analyses, site-related differences in mean oxidative potential or metal composition were evaluated using analysis of variance (ANOVA) with the Games–Howell test to provide robustness against unequal within-site variances when the sample sizes differed between sites. Median values were compared using the nonparametric Mann–Whitney U and Kruskal–Wallis tests. Results from three filter types collected in parallel (TEOM, FDMS base, and FDMS purge) were analyzed using a one-way ANOVA and paired *t* tests with a Bonferroni correction for multiple comparisons.
4. In the remaining analysis, the investigators modeled the contributions of PM_{10} emissions from motor vehicle exhaust, tire wear, and brake wear to the concentration of primary PM_{10} measured at each of the 16 monitoring sites (calculated as the total PM_{10} concentrations measured at each site minus an estimate of the concentration contributed from rural background sites). They calculated the correlations between each of the modeled contributions from exhaust, tire wear, and brake wear to primary PM_{10} and the oxidative potential (expressed per m^3 of air) of the PM collected at each site.

SUMMARY OF MAIN RESULTS FOR PART 2

Characterization of Oxidative Potential and Metal Composition of PM_{10} Extracts

Commentary Table 2 provides an overview of the investigators' conclusions regarding the metals associated with $OP^{AA}/\mu g$ and $OP^{GSH}/\mu g$ results based on their analyses using the crude and the more robust statistical approaches described above. The investigators suggested that, for each measure of oxidative potential, the crude and more robust statistical methods pointed to a similar set of metals. They noted that this set of metals has been associated with tire and brake wear in other studies they had identified (see Table 2 in Part 2 of the Investigators' Report).

For the crude statistical analyses of data from all sites combined, the associations between metal content and measures of oxidative potential were relatively low and were highly variable by site. The top panel of Commentary Figure 4 summarizes the Spearman rank correlations between $OP^{AA}/\mu g$ and individual metals for all sites combined and by individual site; correlations with Cu, Fe, and V were the most consistently positive. The bottom panel shows the analogous results for $OP^{GSH}/\mu g$, which had a different pattern of correlations with the panel of metals; many of the correlations were negative. In the stepwise linear regression analysis (without robust standard errors), the strongest model of the association between $OP^{AA}/\mu g$ and the group of metals shown in Commentary Table 2 had an adjusted R^2 of about 0.27; for $OP^{GSH}/\mu g$, the strongest model had an adjusted R^2 of about 0.31. No quantitative results were reported for the robust statistical methods.

Effect of the CCS on the Oxidative Potential and Metal Content of PM_{10}

The investigators reported that no significant changes in any measure of oxidative potential were observed after the implementation of the CCS in the filters from the Bloomsbury—Russell Square site, the one urban background site within the CCZ. In contrast, statistically significant increases in OP^{AA}/m^3 and $OP^{AA}/\mu g$ were observed at two roadside sites bordering (Westminster—Marylebone Road) and outside (Camden—Swiss Cottage) the CCZ, and in $OP^{GSH}/\mu g$ at one roadside site outside it (Haringey—Town Hall) (results not shown).

Commentary Table 3 qualitatively summarizes the results from the investigators' analysis of changes in the metal concentrations in filter extracts from the six sites in and outside the original CCZ and shows substantial variation in the nature of changes observed. The investigators noted particularly that Cu, Mn, Ni, and Zn decreased significantly at the one background site within the CCZ (Bloomsbury—Russell Square), but that Cu, Ni, and Zn had increased at

Commentary Table 2. Comparison of the Associations Between Oxidative Potential and Metal Concentrations Using Simple and Robust Statistical Methods[a]

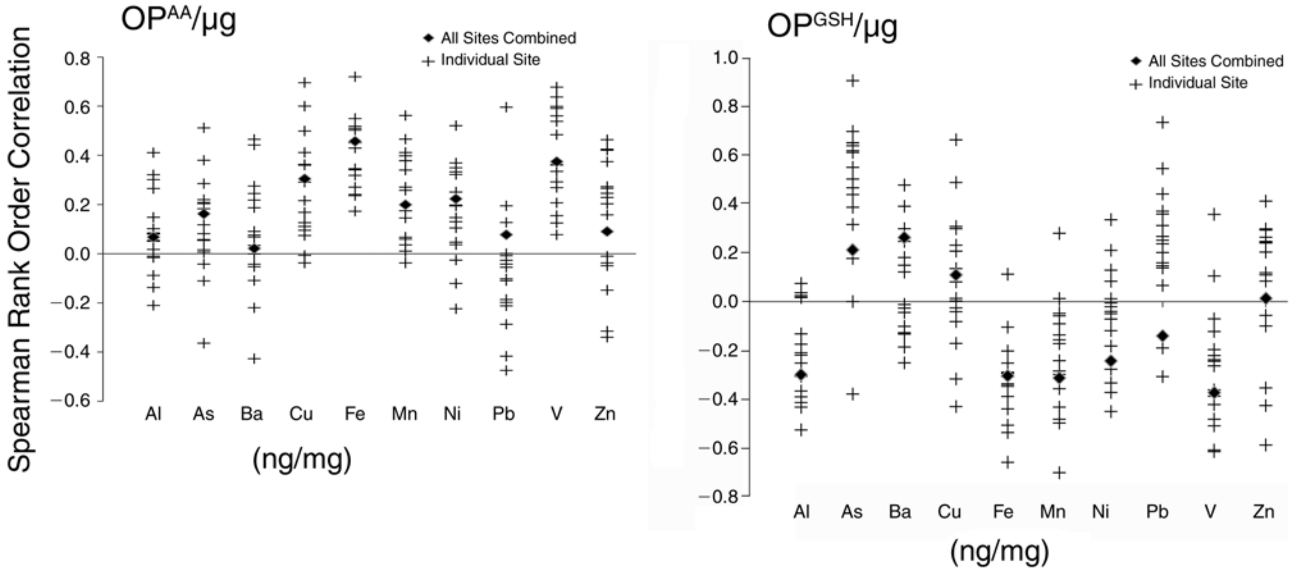
	$OP^{AA}/\mu g\ PM_{10}$		$OP^{GSH}/\mu g\ PM_{10}$	
	Positive	Negative	Positive	Negative
Simple Analyses				
Spearman rank correlation[b]	Al, As, Ba, Cu, Fe, Mn, Ni, Pb, V, Zn		As, Ba, Cu, Zn	Al, Fe, Mn, Ni, Pb, V
Stepwise linear regression[c]	As, Cu, Fe, Mn, Ni, Pb, V, Zn		As, Ba	Al, Mn, Pb, V
Robust Sensitivity Analyses				
Huber–White[d]	As, Cu, Fe, Mn, Ni, V		As, Ba	Al, Fe, Mn, Ni, Pb, V
Generalized estimating equations[c]	Al, As, Ba, Cu, Fe, Mn, Ni, V, Zn		As, Ba	Al, Fe, Mn, Ni, Pb, V
Stepwise regression with robust standard errors	As, Fe	Pb, Zn	As	Pb, V

[a] Correlations reflect data from ~ 730 filters.

[b] All metals are included in the table regardless of the strength of correlation.

[c] Metals that were included in the models that best predicted OP/µg PM_{10} (adjusted $R^2 = 0.27$ for OP^{AA}/µg and $R^2 = 0.31$ for OP^{GSH}/µg).

[d] Huber–White sandwich estimator of standard error. Metals found to be significant ($P < 0.05$).



Commentary Figure 4. Spearman rank-order correlations between oxidative potential expressed as OP^{AA}/µg PM_{10} or OP^{GSH}/µg PM_{10} and the concentrations of individual metals (ng/mg) in PM_{10} filter extracts from 16 sites within and surrounding the CCZ and its Western Extension. Analyzed by individual site (+) and for all sites combined (◆).

Commentary Table 3. Change in Aqueous Metal Concentrations with Introduction of CCS[a]

Monitoring Site	Classification	Al	As	Ba	Cu	Fe	Mn	Ni	Pb	V	Zn
Within CCZ											
Bloomsbury—Russell Square	Urban background	=	=	=	−	=	−	−	−	=	−
IRR–CCZ Boundary											
Westminster—Marylebone Road	Roadside	=	=	+	+	=	−	+	−	+	+
Outside CCZ											
Camden—Swiss Cottage	Roadside	−	=	−	+	+	−	+	−	=	−
Haringey—Town Hall	Roadside	=	+	=	+	=	−	+	=	=	+
K & C—North Kensington	Urban background	=	=	=	=	=	=	=	=	=	=
Greenwich—Eltham	Urban background	=	+	=	+	=	−	+	=	=	+

[a] = indicates no significant change; − indicates significant decrease ($P < 0.05$); + indicates significant increase ($P < 0.05$).

most sites bordering or outside the zone. With some exceptions, Al, As, Ba, Fe, and V remained at comparable levels after introduction of the CCS.

Characterization of Within-City Spatial Variation in the Oxidative Potential of PM_{10}

From their evaluation of spatial variation in PM_{10} oxidative potential across London, the investigators reported that the mean oxidative potential of PM_{10} was higher at roadside monitoring sites than at urban background sites. However, the size and strength of these differences varied by oxidative potential metric; they were statistically significant for OP^{GSH}/µg but not for OP^{AA}/µg, and yet were significant for both OP^{GSH}/m^3 and OP^{AA}/m^3. The investigators reported that roadside sites appeared to have higher fractions (ng metal/mg PM_{10}) of Ba, Cu, and Zn than urban background sites. Background sites had generally higher fractions of Al, As, Fe, and V than roadside sites.

The investigators suggested that the series of experiments designed to provide additional insights into the different contributors to oxidative potential from the filter extracts generally supported a primary role for metals, in particular the transition metals (e.g., Fe, Cu, Ni and V). They inferred from their experiments that Cu content appeared to drive glutathione depletion and Fe was more associated with ascorbate depletion. They found some evidence for activity of the free radical $O_2^{\bullet}$, but not the hydroxyl radical $^{\bullet}OH$.

The experiments to determine the importance of surface-mobilizable Fe and Cu to oxidative potential measurements were not conclusive. The surface-mobilized Fe was slightly more strongly associated with both ascorbate- and glutathione-dependent oxidative potential than was aqueous Fe content determined in the RTLF assay, suggesting the former might be a better indicator of bioavailable Fe. However, the investigators reported that they found no quantitative relationship between the surface-mobilizable Fe and aqueous Fe content of PM determined in the synthetic RTLF assay. In fact, the spatial patterns of surface-mobilizable Fe and aqueous Fe concentrations were opposite to one another; surface-mobilizable Fe was present in significantly higher concentrations at roadside sites than at urban background sites, the opposite of the finding for aqueous Fe. The investigators speculated that this result might be related to differences in the form of Fe contributed from crustal and vehicle-related sources. They found that the surface-mobilizable Cu and aqueous Cu concentrations were more highly correlated and that they therefore displayed similar spatial patterns; both were significantly greater at roadside sites than background sites.

The comparative analysis of oxidative potential in PM_{10} collected from co-located TEOM and FDMS monitors was used to answer concerns about whether oxidatively active volatile or other organic species have been lost during storage or as a result of the high temperatures at which TEOM monitors are operated. The direct comparison, using one-way ANOVA, of PM_{10} extracts from the two sampling methods to deplete either glutathione or ascorbate in the RTLF found few significant differences. In the absence of significant differences, the investigators concluded that there was little evidence using their methodology to suggest that volatile species contribute to the oxidative activity of PM_{10}.

However, they did report substantial variability in the oxidative activity of extracts from TEOM and FDMS filters. Weak, but statistically significant, associations were found in the percent depletion of glutathione between TEOM filter extracts and extracts from both the base ($r^2 = 0.31$, $P = 0.03$) and purge ($r^2 = 0.36$, $P = 0.02$) FDMS filters. No association was found between TEOM extracts and extracts from either type of FDMS filter in their ability to deplete ascorbate. The investigators expressed concern over this lack of correspondence between the two filter systems because FDMS monitors are gradually replacing TEOM monitors in London.

Modeling Vehicle Contributions to Primary PM_{10}

The investigators' modeling analyses suggested that vehicle exhaust was the largest contributor to primary PM_{10}. However, both the absolute and relative contributions from these sources were projected to vary across the 16 sites in the study. Primary PM_{10} generally accounted for a smaller portion of the total PM_{10} measured at each site than estimated contributions from rural background sources.

The investigators could not provide insight into which of the sources of vehicle emissions were likely to contribute most to the oxidative potential of PM_{10} measured at the sites in the study. Vehicle exhaust, tire wear, and brake wear components were each highly significantly correlated with both OP^{AA}/m^3 and OP^{GSH}/m^3. However, because these components were also highly correlated with one another in the models, it was difficult to separate their individual contributions to oxidative potential. They were not correlated with the rural background component of PM_{10}.

INVESTIGATORS' CONCLUSIONS FOR PART 2

The investigators concluded that extracts from PM_{10} collected around London displayed equivalent, or in many cases, greater oxidative potential in the synthetic RTLF assay than equal concentrations of ROFA, used as the positive control. Oxidative potential was characterized in terms of an extract's ability to deplete the antioxidants, ascorbate and glutathione, but not urate in the synthetic RTLF assay. Furthermore, the results suggested that these two antioxidants display differential sensitivity to various metal components of PM_{10}. The analyses of co-located TEOM and FDMS filters also suggested that the non-metal components of PM_{10} do not contribute substantially to the oxidative potential in the RTLF assay, but did not rule out the possibility that they could be oxidatively active.

The investigators were unable to identify a temporal, CCS-related change in the oxidative potential of PM_{10} extracts obtained from TEOM filters in the 2 years before and 2 years after the introduction of the scheme. However, they reported that their city-wide spatial analysis of oxidative potential revealed significant variations in oxidative potential measurements at sites throughout London, with greater oxidative potential associated with PM_{10} sampled from roadside locations than from urban background sites.

The study provided suggestive evidence that PM_{10} derived from tire and brake wear might contribute to the increased oxidative potential of PM_{10} at roadside sites, in particular the transition metals Fe, Cu, Ni, and V. However, due to correlations among contributions to PM_{10} from motor vehicle exhaust, tire wear, and brake wear, their modeling studies were unable to isolate the influence of each of these individual sources of PM_{10} emissions on primary PM_{10} and oxidative potential measured at the sites in their study.

The investigators recommended that studies designed to evaluate the impact on air quality of interventions to reduce traffic should consider other metrics more closely linked to total vehicular emissions and their potential toxicity.

HEALTH REVIEW COMMITTEE'S EVALUATION OF THE STUDY

The London CCS offered an unusual opportunity to investigate the potential impact on air quality of a discrete and well-defined intervention to reduce traffic congestion in the midst of a major city. The investigators had access to London's extensive ambient air monitoring network to support their evaluation. TfL's detailed traffic monitoring system provided data on the actual impact of the scheme on traffic volume and speed. Earlier studies published by members of the investigative team had reported preliminary findings of modest reductions in the number of vehicles entering the zone and had projected declines of about 12% in PM_{10} and NO_x emissions within the CCZ (Beevers and Carslaw 2005). Recognizing that these reductions, coupled with the small area represented by the CCZ in Greater London, could lead to modest changes in air quality, the investigators proposed a multifaceted approach to exploring the impact of the CCS: various modeling techniques, analysis of air monitoring data, and a newly developed assay for oxidative potential of PM.

In its independent evaluation of the study, the HEI Health Review Committee thought that the investigators made a laudable effort to evaluate the scheme's impact. The team undertook a creative stepwise, multidisciplinary approach beginning with updated modeling of potential changes in emissions and air pollutant concentrations. They used the outcome of these modeling studies to help guide the selection and classification of air monitoring sites with which to test their hypotheses about the influence of the CCS on actual changes in NO_x, NO_2, NO, PM_{10}, and CO concentrations. They explored an array of qualitative and quantitative approaches to evaluating the monitoring data, ranging from relatively straightforward comparisons of geometric mean concentrations to development of assays to measure the oxidative potential of PM samples. Nevertheless, their experience also underscores the many substantial challenges that must be anticipated and overcome to successfully demonstrate changes in air quality resulting from interventions of this kind.

MODELING THE IMPACT OF THE CCS ON AIR QUALITY IN LONDON (SPECIFIC AIM 1)

The HEI Review Committee felt that the investigators' efforts to model the impact of the CCS first on vehicle emissions and then on air pollutant concentrations across London represented an important and logical first step. The investigators' stated goals were to "update and verify the tools needed to undertake detailed comparative emissions scenarios and concentration modeling for the CCZ," to use those tools to explore whether and how the CCS would affect air quality, and to guide decisions about next steps in the research. The modeling studies did provide useful insights into (1) the potential spatial patterns of impact of the CCS, in particular the likely impacts closer to roadways, and (2) the relative contributions of roadways, urban background levels of pollutants, and regional air quality to individual pollutant concentration profiles across the CCZ. However, the general finding that the updated models predicted smaller average changes in emissions than those used in the earlier feasibility study underscores the need for a careful evaluation of the model to be used and for its validation before it is used to support regulatory decisions.

The Committee thought the investigators' decision to make use of the LAEI data and existing models from King's College London Emissions and Air Pollution Toolkits was well justified. However, as can be the case when existing data and models are adapted for purposes other than those for which they were originally developed, the Emissions and Air Pollution Toolkits may have had limitations that restricted the investigators' ability to characterize the potential impacts of the CCS on air quality. For example, emission estimates are not necessarily reported for the requisite time scales: estimates for traffic-related sources are expressed only as annual averages of daily totals, and the LAEI projections for nonroad sources are expressed only as annual averages. The CCS, however, is in force only during daytime work hours and therefore would be expected to modify the existing diurnal patterns of pollutant concentrations, especially during the rush hours. To identify an impact of the CCS on this finer temporal scale, hourly estimates of pollutant emission levels would be preferable. In addition, the limited frequency of traffic-count data may also have hampered the investigators' ability to model the impact of the CCS. TfL conducted comprehensive counts of traffic entering and leaving the zone only twice a year in the years up to the introduction of the CCS and four times a year afterward, so daily impacts of the CCS on traffic levels could not be taken into account directly in the models.

The Review Committee also evaluated the investigators' approach to calibrating the air pollution dispersion model and concluded that it further complicated assessment of the model's performance. The investigators' first adjusted the model to fit NO_x monitoring data from a subset of sites before using it to predict NO_x and other pollutant concentrations at another set of sites. The Committee was not convinced that calibration of the model using NO_x would be reliable for prediction of other pollutants, particularly PM_{10}. The Committee would have preferred that the investigators report the model's performance at predicting air pollutant measurements both before and after the calibration and that the steps taken to adjust the model be clearly stated and justified. Simple adjustment of a model does not necessarily deal with the underlying source of bias in the model, may introduce other biases, and ultimately may misrepresent the level of uncertainty in the predictions (National Research Council [NRC] 2007).

The Review Committee thought that the authors could have more critically examined the level of uncertainty in the model predictions and the implications of that uncertainty for later phases of this study and for future studies of this kind. As the investigators acknowledge, their predicted changes in annual average pollutant concentrations after implementation of the CCS were small. For example, the projected net decrease of 1.7 ppb for NO_x within the CCZ over the 2 years following introduction of the CCS accounts for about 3% of the predicted average concentration over the 2 years before the scheme was in place. The analysis of the model's performance (described in Appendix F to Part 1 of the Investigators' Report, available on HEI's Web site) assumes a measurement error of 10% for the monitored values and indicates that the model predicts measured values to within ±30%. Although it was encouraging that this analysis found little bias in the mean predictions of pollutant levels compared with measured values, it is likely that the predicted mean differences in NO_x, $PM_{2.5}$, and NO_2 concentrations are well within the limited estimates of uncertainty and could be further obscured by other important sources of uncertainty, such as larger regional weather patterns.

A comprehensive uncertainty analysis that accounts for the influence of other macroscopic variables on air quality (regional emission changes, long-range transport, meteorologic fluctuations, and other long-term trends) would be ideal but realistically would be quite challenging. Nevertheless, the potential role of such factors and the ability of the models to deal with them should be carefully considered in the design of a modeling approach and in the evaluation of its results.

The Committee thought that the most useful outcome of the modeling studies was to highlight the need for more ambient air quality monitors. In particular, the analyses showing the impact of the CCS on concentrations along a transect across the CCZ highlighted the importance of having more monitors both near the roadside, where exposures were anticipated to be highest, and at urban background locations because of the substantial influence of regional air quality on pollutant concentrations in the city.

EVIDENCE FROM MONITORING DATA ON THE IMPACT OF THE CCS (SPECIFIC AIMS 2 AND 3)

The Review Committee thought that the process for establishing the CCS Study Database was generally sound and provided a solid basis for collection of the pollutant concentration data. One potential limitation of the process was the investigators' choice to apply the 75% data-capture rate across all 4 years of data collection, rather than to each 2-year period before and after CCS implementation. The result was that the percentages of the pre- or post-CCS period for which monitoring data were available, the average sampling intervals, and the numbers of filters varied among sites, which led to potential biases and uncertainties that were not assessed.

Despite the overall quality of the process for establishing the CCS Study Database, the Committee agreed with the investigators that there were substantial limitations in the number of adequate monitoring sites to test the impact of the CCS from the outset of the project. For example, there were no roadside monitors and only one urban background monitor for PM_{10} within the original CCZ. Even after expanding the set of monitors to include the planned Western Extension of the CCZ, there was only one roadside site and three urban background sites within the CCZ with which to monitor PM_{10}. They also acknowledged two problems that surfaced with the PM_{10} data for the one critical urban background monitoring site where it was measured within the CCZ, Bloomsbury—Russell Square. Peak PM_{10} concentrations observed between March and May 2002, were traced to emissions from a nearby building site. Furthermore, the time series for this site was missing PM_{10} data during the crucial time period from June 2002 to March 2003 (just before CCS implementation) because of an equipment failure. Despite these important limitations, however, the Bloomsbury—Russell Square data were still included in the CCS Study Database and thus complicated the interpretation of any analyses that relied on them.

The Review Committee also commented on the investigators' analyses of the pollutant concentration time-series data, in particular on their characterization and accounting for factors other than the CCS that might have a strong impact on air quality. Meteorologically induced variation plays a dominant role in masking air quality responses to emission changes in general and, as the investigators acknowledged, considerable meteorologic influence on Greater London's air quality was evident in the CCS data. They generally observed evidence of strong seasonality in the CO, NO, and NO_x concentrations at all sites (reported in Appendix G to Part 1 of the Investigators' Report). In addition they noted that in the first year of the scheme (2003) a weather inversion caused an increase in regional background concentrations of PM_{10} that may have obscured any local air quality improvement associated with the CCS.

The investigators' decision to match daily data from monitoring sites within the CCZ to those 8 km from the zone's center, and to adjust the ratio of the post- to pre-CCS geometric mean concentrations of pollutants at CCZ sites by the comparable ratio at sites in the control area was a pragmatic effort to account for regional air pollution trends with the data at hand. However, these controlled ratios are not straightforward to interpret and ultimately are not the preferred approach to dealing with regional changes in pollutant levels that might have occurred over the course of the study. The Committee thought that a preferable model might have included fixed site and site class (within zone, boundary, background), season, and year as fixed effects, and random effects for weather. The quantity of interest would be the interaction effect between year and site class (see, for example, Sampson and Guttorp 1990). Ideally, the Committee would have liked to have seen an approach in which meteorologic trends were analytically removed from the data (see, for example, Rao and Zurbenko 1994; Rao et al. 1995; Kuebler et al. 2001; Porter et al. 2001); the detrended data might then have been more successfully used in both the main and the exploratory analyses.

The Committee acknowledged that such modeling approaches can involve additional statistical complexities that are also subject to interpretation. Thus, the investigators' simpler approach, in which they sought to account for potentially confounding factors in their study design, was reasonable. They assumed that meteorology, trends in vehicle emissions, and other temporal patterns in regional pollution should act similarly across all of London and the South East of England and therefore would affect equally the CCZ and the surrounding areas. By making comparisons in temporal trends within the zone with trends over the same time period in the control area, the investigators were able to control in some part for potentially confounding factors, although additional analyses would likely be necessary to verify that interpretation.

Finally, the Committee remained concerned that the investigators' analysis and discussion of the temporal changes in geometric means at individual sites in the study never directly dealt with potential spatial and temporal autocorrelation in their data; that is, the problem that the monitoring sites are spatially clustered and that the measurement data are correlated over time. Although the authors acknowledge that autocorrelation may exist, they have not fully accounted for the extent to which it may undermine any conclusions that can be drawn from their simpler approaches.

ADDITIONAL EXPLORATORY ANALYSES

In short, the Committee thought the three exploratory approaches were creative and agreed with the investigators that all three methods need further development before being used in future studies.

The use of ethane concentrations to help assess meteorologic dispersion was an interesting approach, but important uncertainties remained unresolved. The Committee noted that ambient ethane not only comes from natural gas leakage, but is also emitted by vehicles fueled either by natural gas or by gasoline and by residential and commercial heating systems. Since heating may also be meteorologically driven, data on emissions of ethane mass by source might have been useful to examine.

The effort to apply the CUSUM technique to look for changes in air quality in the CCS data was creative. However, without an analytic approach for dealing with seasonal and other meteorologic trends in the data, it was unrealistic to expect that small changes in air quality could be detected. Furthermore, a key issue was that autocorrelation in the monitoring data would violate the assumption in the CUSUM technique that observations are independent and identically distributed. CUSUM procedures for dealing with autocorrelated data, such as the CCS data, have more recently become available (Kirch 2007).

The use of bivariate polar plots to provide insight into the direction and characteristics of primary emission sources is very interesting. However, a number of factors led the Committee to be uncertain about whether this analysis had been sufficiently designed and tested to demonstrate what it had set out to show. For example, the basis for selecting the particular spatial correlation structure to krige the polar plots and why it differed from more standard approaches to spatial analyses of air quality in the statistics literature were not well justified. Furthermore, a clearer articulation of the model's potential prediction error is necessary to help evaluate the power of the model to detect the impact of projected changes in source characteristics.

OXIDATIVE POTENTIAL OF LONDON'S PM (SPECIFIC AIM 4)

The Review Committee thought the investigators' attempt to characterize the oxidative potential of PM was an interesting and potentially illuminating study. However, the largely inconclusive findings reflect limitations of the monitoring network and data, as discussed in the previous section, as well the fact that the synthetic RTLF model of oxidative potential was in an early stage of development.

The general concept of looking at a toxicologically relevant measure of the aggregate PM mixture is appealing. PM is a complex mixture and efforts to predict its overall toxicity on the basis of the properties of individual components have challenged investigators for many years. At the time this study was proposed, the oxidative stress pathway was emerging as an important hypothesis for the health impacts of exposure to PM, so the investigators' choice to focus on a measure of PM's ability to trigger this pathway was logical.

The specific approach that the investigators took to characterizing oxidative potential, based on a synthetic model of lung fluid, was also conceptually sound. A number of models of oxidative potential were being investigated at the time the CCS study was initiated but none, including the RTLF model, had been fully tested outside the laboratory. Although the RTLF model had been tested with different PM sources (Mudway et al. 2004, 2005), the London CCS study was one of its first large-scale applications in a major city. It was not surprising that a number of details had not been fully worked out and that additional model development was necessary as part of this study.

One objective of the study was to assess whether or not implementation of the CCS had an effect on the oxidative potential of London PM. The overall result was that the investigators could not find a definitive impact of the CCS. This finding was not surprising given limitations in the filter data and reliance on statistical analyses that were not designed to take into account the potential impacts of long-term meteorologic trends or of spatial–temporal autocorrelation in the filter data (e.g., multiple filters from the same small number of sites).

The results of the investigators' spatial analysis of PM_{10} oxidative potential that show greater activity in the samples from roadside monitors compared with those from urban background sites offers one explanation for the apparent lack of a CCS impact. No roadside monitoring sites existed within the original CCZ (except one curbside site at the boundary) and only one was added for the purposes of this study. So if the impact were to occur primarily at roadsides, there were simply not enough monitors in the right locations to detect it.

The Review Committee thought the most interesting result was the modest suggestion that metals associated in other studies with tire and brake wear (As, Ba, Cu, Fe, Mn, Ni, V, and Zn) might contribute to the oxidative potential levels observed. The authors' conclusion was primarily based on the results of simple correlation and regression analyses of data from all sites combined, without corrections for autocorrelation or multiple comparisons, although those results were corroborated to some degree by the sensitivity analyses using more robust statistical techniques. However, none of the measures of association were particularly strong.

It is also possible the uncertainties in the RTLF method itself contributed to the finding. The investigators had made the pragmatic decision to use reported and ratified pollutant mass levels (from measurements during sampling) for the 730 filters rather than mass recovered from the filters directly. The Review Committee noted the poor correlation between the ratified PM mass and the recovered PM mass for a subset of 50 filters in a quality assurance study conducted by the investigators. Filters were also examined by scanning electron microscope to address the Research Committee's concerns about the completeness of extraction and its impact on the filter surface. Although microscopic evaluations of the filters suggested that extraction was complete and that the filters were intact, the recovered mass levels ranged from 50% to 200% of the ratified mass levels, which the Review Committee noted could explain at least some of the difficulty in detecting significant differences in the spatial and temporal analyses of the filter record.

A number of unresolved questions remain about the interpretability of the RTLF oxidative potential findings in this study. As the authors acknowledge, the oxidative potential results are likely to provide an incomplete picture of the potential toxicity of London air pollution. The need to rely on archived PM_{10} filters meant that the measures of oxidative potential reflected only the stable components of PM_{10} — metals. The potential contributions of organic compounds (for example, the oxy- and nitro-polycyclic aromatic hydrocarbons and quinones that have been implicated in the oxidative activity of PM by other investigators; Biswas et al. 2009; Cho et al. 2005) could not be measured. The results of the analyses of PM from the FDMS filters, which are collected at somewhat lower temperatures than TEOM filters, might be interpreted to suggest that these other heat-sensitive PM components are not major contributors to the oxidative potential of London's PM, but the Review Committee did not think they were conclusive. The potential role of gaseous pollutants in the overall toxicity of London's air pollution also remains unaccounted for by this assay.

The Review Committee shares the investigators' concern about the poor correlation between the antioxidant depletion rates reported for the TEOM filter extracts and the FDMS filter extracts. The reasons for this finding are not entirely clear, but one possibility may be the investigators' decision not to normalize the depletion rates by PM mass. Unless the discrepancies are resolved, they raise potential concern for future studies using the RTLF method as a tool for characterizing the oxidative potential of ambient PM over time periods that span the use of the different monitoring methods.

Further research is necessary to develop and interpret the results of oxidative potential metrics; the somewhat ambiguous findings encountered by the Kelly team are not unique. At about the same time as the CCS study, Künzli and colleagues (2006), including members of the Kelly team, characterized the reduction-oxidation (redox) activity of $PM_{2.5}$ in 20 European cities using on the basis of its ability to generate hydroxyl radicals in the presence of the oxidant hydrogen peroxide, and its ability to deplete ascorbate and glutathione in the RTLF model. They then explored relationships between these measures of oxidative activity and different characteristics of PM — light absorbance, total $PM_{2.5}$ mass and the mass concentrations of individual elements. That study also found low correlations between oxidative activities and these other characteristics of $PM_{2.5}$ and could not identify any one sufficient measure of $PM_{2.5}$ redox activity.

The development of assays that capture and explain the oxidative potential of ambient PM continues to be an active area of research. Other investigators have proposed different assays for measuring the oxidative activity of PM in acellular models (Li et al. 2003; Cho et al. 2005; Venkatachari and Hopke 2008; Biswas et al. 2009) as well as in cellular models (e.g., Hu et al. 2008). However these models differ with respect to the size (e.g., PM_{10}, $PM_{2.5}$, ultrafine, or nanoparticles) and components of the PM targeted. For the more commonly used acellular dithiothreitol assay, the protocols are not always standardized across laboratories, which makes comparison of the results challenging. No standard methods have yet been agreed upon by the scientific community.

Ultimately, the relationship between oxidative potential as measured in the synthetic RTLF or other assays and the ability to trigger events further along in the oxidative stress pathway leading to human health effects warrants further exploration if it is to be a useful exposure metric in epidemiologic studies. In the same study of diesel exhaust exposures in human subjects that contributed to the development of the synthetic RTLF assay, Mudway and colleagues (2004) reported evidence that suggested that the air–lung interface in healthy subjects was capable of meeting the oxidative challenge posed by diesel exhaust at ambient concentrations. They found neither airway inflammation nor antioxidant depletion (ascorbate, glutathione, or urate) 6 hours after exposure and found an increased flux of reduced glutathione into the bronchial and nasal airways. At a recent workshop on research into methods to assess oxidative potential, researchers recognized the value of acellular assays as potential screening tools but recommended that studies move toward greater use of cellular and other biologically relevant assays (Ayres et al. 2008).

CONCLUSIONS AND IMPLICATIONS FOR RESEARCH ON THE EFFECTIVENESS OF AIR QUALITY INTERVENTIONS

Ultimately, the Review Committee concluded that the investigators, despite their considerable effort to study the impact of the London CCS, were unable to demonstrate a clear effect of the CCS either on individual air pollutant levels or on oxidative potential of PM_{10} in this study. The investigators' conclusion that the primary and exploratory analyses collectively indicate a weak effect of the CCS on air quality should be viewed cautiously. The results were not always consistent and the potential uncertainties surrounding them were not always clearly presented, making it difficult to reach definitive conclusions.

In conducting this valuable effort, Kelly and colleagues encountered a set of issues that have come to exemplify the general challenges facing health outcomes research (van Erp and Cohen 2009). One is the difficulty of detecting significant air quality improvements from an intervention against a backdrop of broader regional and meteorologic variations in background concentrations of pollutants. A second is that other changes occurring at the same time (e.g. the introduction in response to a separate rule of more filter-equipped diesel buses) may also affect air quality and obscure effects of the intervention being studied. The third is that institutional or behavioral changes in response to an intervention, not all of which may be fully anticipated, can also partly offset the possible gains. For example, although access to public bus transport was improved as part of the scheme, traffic count data from the first year indicated increased numbers of trips into the inner city of London by taxis and other vehicles not subject to the daily charge; traffic in the ring roads surrounding the zone also appeared to increase.

Similar challenges have vexed other health outcomes studies. In their extended analysis of the impact of actions taken during the 1996 Summer Olympic Games to improve traffic flow in downtown Atlanta, Georgia, Peel and colleagues found that the previously reported decrease in O_3 concentrations was regional in nature, making it unlikely that changes in air quality could be attributed to the traffic control measures (Peel et al. 2010). In Beijing, China, several measures were taken to reduce emissions from traffic and stationary sources during the Summer Olympic Games in 2008. Although air pollution measurements suggested that levels of several pollutants declined during that period, several other factors appear to have contributed to the observed changes, including changes in regional industrial sources and meteorologic patterns (Wang et al. 2008).

The experiences in these studies demonstrate the importance of establishing at the outset the extent to which the actions are likely to improve or have actually improved ambient air quality before health studies are contemplated. In this case, original modeling suggested a potential 12% reduction in emissions of NO_x and PM_{10} within the CCZ in the first year following introduction of the scheme. Although modeling in this study suggested average emissions of NO_x and PM_{10} could be reduced by a greater amount in the zone over the 2 years following the scheme, the estimated impact on NO_x, NO_2, and PM_{10} concentrations was projected to be very small. Studies should also be adequately designed to explore the basis for observed changes by evaluating multiple time windows surrounding the intervention, by comparing changes at the study location with those in the surrounding areas, by employing analytic methods to remove the meteorologic trends in the data, and by including analytic approaches for dealing with the spatial and temporal autocorrelation in the monitoring data.

Without sufficient changes in air quality, health studies are unlikely to have adequate statistical power to detect any effects on health. It is important to recognize, however, that defining a "sufficient" concentration reduction for a study must also take into account the other determinants of the study's power — exposure misclassification, size and underlying susceptibility of the study population, other sources of environmental pollution that affect human health, and size of the anticipated health response (Health Effects Institute 2010).

A related issue highlighted by Kelly and colleagues is the importance of evaluating early in the design phase whether existing monitoring networks are adequate (in terms of the number and location of monitors and the pollutants covered) for the purposes of measuring a change in air quality. This issue is especially important when studying the effect of traffic measures, for which both roadside and centralized urban background monitors may need to be added to the network. The presence of only one roadside monitor within the CCZ made it very difficult to study the impact of traffic-related changes on air quality. These limitations were a factor in the investigators' efforts to develop a broader monitoring network with which to characterize spatial patterns of PM oxidative potential within London and to provide baseline data for future studies of the Western Extension of the CCZ, which went into effect in February 2007, and of the Low Emission Zone, originally scheduled to be implemented in 2008. (Since this study was completed, plans to remove the Western Extension from the CCZ were set in motion in 2008 [Milward 2008] and it was officially removed in January 2011).

The second part of this study introduced an RTLF assay, a novel method to measure the oxidative potential of PM, which is intended to represent the aggregate ability of an exposure to PM to trigger oxidative stress. Coupled with several analyses designed to tease out possible PM components, in particular water-leachable metals that have been associated with PM from tire and brake wear in other studies, the investigators hoped to develop another tool with which to characterize changes in London PM after traffic or air quality interventions. It was the first major application of this method in a large urban area.

Use of the RTLF assay, or other methods to assess oxidative potential, to represent the potential toxicity of exposure to a complex mixture such as ambient PM_{10}, is an intriguing concept. However, the same limitations of the first part of the CCS study constrained the findings in the second — the small area of the CCS within the Greater London area, the small numbers of monitoring sites in and around the CCZ, the differential availability of filters among monitors over time and space, and the absence of a clear analytic plan for dealing with spatial and temporal autocorrelation in the data. In addition, inherent uncertainties in the RTLF assay also likely contributed to difficulties in discerning clear differences among sites. Its use in this study was largely exploratory, particularly in those experiments designed to distinguish the contributions of individual elements or classes of compounds to oxidative potential in PM from archived filters. Further work is also necessary to solidify the RTLF assay's role as an indicator of potential human toxicity.

The investigation of the impact of the CCS by Kelly and colleagues represents a creative effort to explore a subtle change in air quality associated with a complex intervention to reduce traffic congestion. These investigators, in essence, covered the first three steps of the Outcomes Evaluation Cycle; they (1) provided evidence that the intervention or controls have in fact been put in place, (2) modeled the potential impact of the intervention on emissions, and (3) assessed whether the intervention had resulted in improved air quality. Their study offers many lessons for future studies of interventions that are expected to influence air quality, whether intentionally or not. In particular, it adds to the growing body of evidence confirming the value of establishing the extent to which interventions have improved, or are likely to improve, ambient air quality before health studies are contemplated. The investigators had the opportunity to take some of these lessons into account in their second HEI-funded study, a baseline evaluation of the proposed London Low Emission Zone (Kelly et al. 2011).

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