



APPENDIX AVAILABLE ON REQUEST

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Atmospheric Transformation of Diesel Emissions

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Appendix C. Detailed Description of the Results Obtained During EUPHORE Campaigns – Chemistry of the Atmospheres

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APPENDIX C

C. DETAILED DESCRIPTION OF THE RESULTS OBTAINED DURING EUPHORE CAMPAIGNS – CHEMISTRY OF THE ATMOSPHERES.

1. CHAMBER ATMOSPHERE COMPOSITIONS

During the first campaign in winter 2005, the diesel engine was new and had been in operation for only a few hours prior to starting the exposures. This may be the reason that some of the data obtained during this campaign, most notably diesel particle size distribution and chemical composition, are slightly different than in the following campaigns, as described below. In addition, all experiments in winter 2005 were performed without a NO_x denuder (the problem with excess NO_x became apparent during this campaign). During the summers of 2005 and 2006 some of the dark experiments were repeated with and without the NO_x denuders for comparison purposes.

This Appendix describes the results of dark (Section 1.1) and light (Section 1.2) exposures carried out in the EUPHORE chamber. Both continuous and time integrated data are discussed in separate sub-sections. Continuous data were measured directly from the chamber during all exposures. Time-integrated data include chemical speciation data that were obtained at the DRI laboratories from the samples collected at the end of each exposure, as described in Section 3 of the main report. The samples collected with the XAD diffusion (also called Gundel) denuder were analyzed for PAH, nitro-PAH and alkanes (all samples) selected polar compounds and hopanes/steranes (selected group of samples). The extracts from the XAD-coated denuder section, TIGF filter and XAD cartridge were analyzed separately, as described in Section 3.6 of the main report. In addition, quartz filter samples collected at the end of each exposure were analyzed for mass, OC, EC, sulfates and nitrates.

The concentrations of all species in time-integrated samples collected from all chamber experiments are provided in an electronic form and are available from the HEI website as Appendix F (summer exposures) and G (winter exposures) upon request. The concentrations of all organic species are calculated in relation to the elemental carbon concentration, EC (i.e. microgram or nanogram of compound per milligram of EC). The inherent assumption in this normalization procedure is that EC mass will remain unchanged while atmospheric transformations of speciated organic compounds take place within the chamber atmosphere. In other words, individual organics can either be produced as secondary organic aerosol (SOA) or be consumed in transformation reactions. These processes can change the total PM mass, while leaving EC unperturbed. An additional assumption is that the wall losses for organics and EC are approximately the same. In cases when more than one run was performed for a given type of atmosphere, the data are averaged and standard deviations between runs are provided.

1.1 Dark Exposures

1.1.1 Continuous Data

Table 1 lists the initial conditions for all dark exposures performed during the 2005 and 2006 campaigns. The conditions reported here are immediately after injection, and do not reflect aged emissions. Most notably, the removal efficiency of the NO_x denuder used in 2006 did allow for lower NO_x levels (e.g. Dd06s_1 = 7ppb and Dd06s_2 = 35ppb). The *Co/GROG* denuder removes NO_x very efficiently (over 99%), and concentrations in the chamber were in the range of 25-50 ppb for 30 – 35 minute injection times (2006). Without the NO_x denuder, these concentrations would be in the 7 – 8 ppm range. The high mass concentrations of PM in the winter 2005 campaign could be a function of both engine age, and lack of denudation associated particle losses. It is important to note the relative consistency of temperature and water vapor in all exposures.

SMPS data

The post-injection diesel particulate matter (DPM) levels derived from SMPS data are shown in Table 2. The median and mean diameter values with the experimental maximum mass concentration reveal similar aerosol loadings for the individual campaigns. The consistently higher median and mean values for experiments in summer 2005 and 2006 with the NO_x denuder versus experiments in winter 2005 without the NO_x denuder are apparent from this table. However, this is probably due to the effect of the diesel engine getting older, and not due to the use of the NO_x denuder. Figure 1 shows the SMPS data collected during dark diesel runs in May 2006, with (A) and without (B) NO_x denuder (runs D06s_1 and Dd06s_1). The addition of the large volume NO_x denuder body has not changed the diesel particle size distribution significantly.

In general, the DPM concentrations in the chamber were reduced by denudation (with equivalent injection times). For example, without the NO_x denuder, we obtained ~ 60 µg/m³ of DPM in the chamber after a 10 minute injection, while only 40 – 50 µg/m³ was achieved following a ~30 min injection with the denuder (2006 campaign). However, the DPM concentration depends on the engine loading and small differences in the loading over the course of the diesel exhaust injection can make a significant difference for DPM values. The dynamometer loading tends to decrease over the course of an injection, so a longer injection time results in a lower than predicted particle concentration (see Appendix B for further discussion).

Evaluating the pre-sampling DPM values, reveals significant particle loss due to dilution, settling, and chamber wall impacts during the ~5 hour emissions aging period. It is important to note that the D05w_4 experiment did result in the highest pre-sampling and maximum DPM. As discussed below, the sample collected from this exposure shows unusual chemical and toxic properties. In general the 2005 winter campaign DPM engine output was significantly higher than the summer campaigns. For example, an average winter mass concentration of 13.4µg/L (+/-19%) was calculated utilizing chamber mass

loadings immediately following diesel injection. In contrast the summer 2006 DPM injection concentration averaged at 10.1µg/L (+/-10%) without the NO_x diffusion denuder in-line (see Appendix A and B for more detail).

Peroxyacetylnitrate, nitrous acid and formaldehyde

Table 3 is an overview of the dark experimental HONO, PAN, and HCHO results for all 3 EUPHORE campaigns. The winter 2005 FTIR HONO results appear to be consistent for the D05wN replicates. It is clear that the higher mass dark experiments (D05wN_5 and D05wN_6, see Table 3 at the main report) resulted in a higher HONO production. This is also consistent with the 2005 summer long path absorption photometer (LOPAP) data. HONO production is dependent upon several heterogenous reactions, which take place on the surface of diesel soot and other atmospheric aerosols (Finlayson-Pitts and Pitts 2000). As surface-bound organic reactants are consumed, the soot particle surface is oxidized leading to an altered surface chemical composition, which is increasingly hydrophilic. It has been postulated that HONO can be a significant gas-phase product when NO_x and fresh diesel exhaust interact (Arens et al 2001). The implications for particle-phase toxicity are not well understood.

Volatile Organic Compounds (VOC)

Based on the in-situ GC/MS data, we noticed that the NO_x denuder (*Co/GROG*, 2006 version) seems to remove some aromatic VOCs, such as alkyl substituted benzene derivatives. However, since our diesel engine is equipped with an oxidation catalyst, the engine-out VOCs concentration is very low even without the denuder. For example, in 2005 (both winter and summer), canister samples taken from the chamber at the end of the dark aging period revealed that VOC concentrations (C₂-C₁₁) were <10 ppb (sum), with individual compound concentrations <0.1 ppb (e.g. benzene, toluene, xylenes). In the summer 2005 campaign, use of the honeycomb NO_x denuder appeared to drop VOC levels to near detection limits (ppt), with compound sums for equivalent injection times <1 ppb. In the summer 2006 campaign, *in-situ* GC/MS data revealed that VOC levels were in the <10 ppb level (with and without the NO_x denuder) and addition of the VOC mixture was undertaken (see Section 3 in the main report). For identified compounds (2006 summer), it appears that the use of the *Co/GROG* denuder did not significantly impact VOC concentrations (e.g. benzene, toluene, xylenes). Yet the reported VOC levels were near detection limit whenever additions were not made, and quantified differences fall within instrumental sensitivity parameters.

1.1.1.1 Time-integrated Data

The initial conditions for all dark exposures are listed in Table 1. As explained in Section 3.5, most of the dark exposures were performed in winter 2005 with several replicate exposures in summers of 2005 and 2006, both with and without a NO_x denuder that was used to introduce diesel exhaust to the chamber. Note that different NO_x denuders were used in summer 2005 and 2006 (honeycomb versus annular).

Organic/Elemental Carbon and Inorganic Ions.

Samples for OC/EC and nitrate and sulfates measurements were collected on quartz filters at the end of most exposures, usually for 2-3 hours to obtain sufficient mass for these analyses. Table 4 shows the total OC, EC, total carbon (TC), sulfates and nitrates, whereas detailed data, including all OC and EC fractions are provided in an electronic form and are available in Appendix F and G from the HEI website.

Figure 2 (upper panel) shows the OC and EC fractions for these samples (in $\mu\text{g}/\text{mg}$ PM). Carbon fractions in the IMPROVE method correspond to temperature steps of 120°C (OC1), 250°C (OC2), 450°C (OC3), and 550°C (OC4) in a nonoxidizing helium atmosphere, and at 550°C (EC1), 700°C (EC2), and 850°C (EC3) in an oxidizing atmosphere. IMPROVE TOR method uses variable hold times of 150-580 seconds at each heating stage so that carbon responses return to baseline values (Chow et al, 1993). Some very polar or oligomeric/polymeric organic compounds pyrolyze when heated during the oxygen-free stage of the analysis and produce additional EC, which is defined as pyrolyzed organic carbon (POC). The formation of POC is monitored during the analysis by the sample reflectance and is added to total OC. In case of dark exposures POC was negligible, but it was important for some light exposures, as shown below.

As shown in Figures 2, there is a difference between diluted diesel exhaust aged in the dark chamber in winter 2005 and summer 2005 and 2006. The four winter 2005 samples (D05w_1, _2, _3 and _4) have higher TC and OC contents than summer 2005 (Dd05s_1 and _2, introduced with NO_x denuder) and 2006 (D06s_2 and _3, without NO_x denuder and Dd06s_2, with NO_x denuder). Winter 2005 samples have much higher OC1 fractions that are comprised of mostly volatile organic carbon. OC/EC ratio is also much higher, especially for sample collected for toxicity testing (D05w_4). This is most probably due to the fact that the modern Ford diesel engine used for these experiments was new in the winter 2005 with only a few hours of engine running prior to the beginning of winter campaign. The engine was run for over 40 hrs from winter to summer 2005 and was much more stable in summer 2005 and 2006 campaigns, as evident from more uniform OC/EC ratios.

Figure 2 (lower panel) shows the TC, sulfates and nitrates contents (in $\mu\text{g}/\text{mg}$ PM) in all dark exposures. Samples collected from NO₃ radical (from N₂O₅ decomposition) reactions with diesel exhaust (D05wN_2, _4, and Dd05sN_1, _2) have higher sulfates and nitrates contents than aged diesel exhaust. This is consistent with higher oxidative conditions in the chamber during these experiments.

Polycyclic Aromatic Hydrocarbons (PAH)

As described in the Method section (Section 3.6 in the main report), organic species were collected with the XAD-coated diffusion denuder (“Gundel” denuder, Gundel et al, 1995) to obtain information regarding phase distribution of organics. The flow rate through the denuder was calculated to assure that three-ring PAHs, starting from phenanthrene, are retained on the XAD-coated denuder section (Zielinska et al,

2004). Thus, the PAH more volatile than phenanthrene (i.e. naphthalene and methylated naphthalene) may exhibit some break-through when sampling with the XAD-denuder. In this case, the PAH would be collected on the XAD cartridge that follows the TIGF filter. The concentrations of species collected on the filter and XAD cartridge was summed together, to account for the volatilization of semi-volatile (SV) compounds from the filter (Gundel et al, 1995, Zielinska et al, 2004).

Figure 3 shows the distribution of lower molecular weight (mw), mostly gas-phase PAH (LPAH: naphthalene, biphenyl and their methyl-, dimethyl- and trimethyl-derivatives), semi-volatile PAH (SVPAH, three and four ring PAH) that are distributed between gas- and particle phases, and particle-associated PAH (PPAH, five- and 6-ring PAH) in all dark exposures. To make the figure simpler only the most abundant PAH are shown and the multiple runs from the same atmospheres are averaged. Whereas LPAH and SVPAH are distributed between gas- (denuder) and particle- (filter+XAD) phases, the PPAH are present only on the particle phase – their concentrations on the XAD-coated denuder section were below detection limits. As it can be seen from this figure, the winter 2005 dark exposures are different from subsequent exposures, as far as concentrations of PPAH is concerned. Clearly, the high mw, particle associated PAH are much more abundant and more variable for these exposures. As mentioned above, this may be due to the diesel engine being brand new in winter 2005. For summers 2005 and 2006, the concentrations of PPAH are very low. Also, for the dark NO₃ radical exposure in summer 2006 (with NO_x denuder, Dd06sNV), naphthalene was added to the chamber (1.9 mg which resulted in 9.5 µg/m³ concentrations in the chamber) which explains much higher naphthalene concentration in this exposure.

There is also a difference between the gas- and particle- phase distribution of SVPAH in the 2005 and summer 2006 campaigns. It seems that there are higher gas-phase concentrations and lower particle-phase concentrations of SVPAH in 2006. This may be due to the differences in ambient temperature during exposure and collections of samples (see Table 1 for initial temperature conditions). There is also higher breakthrough of volatile naphthalene and methyl naphthalenes through the XAD denuder section – thus these PAH are abundant on the filter + XAD section, which is clearly an artifact.

Table 5 shows the sum of the concentrations for LPAH, SVPAH and PPAH and the particle mass measured from the filter for each dark exposure. As mentioned above, the PAH concentrations are normalized to the elemental carbon mass.

The concentrations rank in the order LPAH >>SVPAH>>PPAH. For NO₃ radical exposures the LPAH concentrations are depleted (with exception of Dd06sNV, where naphthalene was added), due to the gas-phase reactions of these PAH with NO₃ radicals.

Nitro-PAH

Figure 4 shows the most abundant nitro-PAH concentrations in all dark exposures (see Table 7 in the main report for the list of nitro-PAH measured and Appendix F for their concentrations). As mentioned above, the multiple runs from the same atmospheres are averaged. Very high concentrations of 1-nitronaphthalene (1NN) distributed between gas- (denuder) and particle- (filter+XAD) phases are observed for the Dd06sNV exposure, where 1.9 mg of naphthalene was added to the chamber atmosphere. For the remaining exposures, 1NN is also the most abundant nitro-PAH observed. Again, winter 2005 exposures show much higher and more variable nitro-PAH concentrations than subsequent summer dark exposures, most probably due to the differences in engine age.

Alkanes and Cycloalkanes

Samples from both summer campaigns (2005 and 2006) were analyzed for alkanes and cycloalkanes. Figure 5 shows n-alkanes (from n-tetradecane, nC14 to n-tetracontane, nC40, upper panel), n-alkane-cyclohexanes (from n-heptylcyclohexane, cC13 to n-nonadecylcyclohexane, cC25, middle panel) and iso-alkanes (norfarnesane, iC14, farnesane, iC15, norpristane, iC18, pristane, iC19 and phytane, iC20, lower panel) in summer 2005 and 2006 dark exposures (in microgram per mg of EC). These concentrations are much higher in 2006 than 2005 samples. This may be due to a much longer diesel engine running time (and overheating) in 2006 and thus higher contribution of unburned diesel fuel to the exhaust. The gas-phase concentrations of n-alkanes, n-alkane-cyclohexanes and iso-alkanes are depleted in the NO₃ radical reactions, both with and without NOx denuder.

Hopanes, Steranes and Polar Compounds

Only samples from the summer 2006 campaign were analyzed for hopanes/steranes and only selected samples from both light and dark exposures were analyzed for polar organic compounds (POC). These data are shown in the main body of the report, Section 4.1.

1.1.2 Light exposures

1.1.2.1 Continuous data

All light exposures were done in summer 2005 and 2006 campaigns. Note that two different NOx denuders were used in summer 2005 and 2006, as explained in Section 3.4 of the main report.

Table 6 lists the initial conditions for all light exposures performed during these campaigns. The highest NOx level observed (L05s_2) during the light experiments, was from a 10-minute injection without NOx denuder during the summer 2005 campaign (1844 ppb). This injection produced a relatively high PM concentration (37.1 µg/m³), which is typical for ambient urban environments (Rees et al 2004). In 2006, a 10-minute

injection with the newly designed *Co/GROG* denuder (Ld06sT_2) produced a similar PM concentration, but significantly lower NO_x. The slight shift to higher median and mean particle diameters (Table 7) with the latest denuder may be a function of longer exhaust transit time, preferential scavenging of small particles or the diesel engine becoming older. Note the consistency between all experimental replicates (median, mean), and the similar post-injection/pre-sampling variability.

Table 8 displays all light HONO, PAN, HCHO, and ozone maximum *in-situ* data for all 3 campaigns. The highest HONO production occurred during the L05s_2 experiment (mentioned above), where high NO_x and PM provided the most appropriate conditions. The maximum ozone production in 2006 did occur in a DE + OH + VOC experiment on 06/07/06 (Ld06sFV_1). Once corrected for dilution losses during chamber experiments (with SF₆ derived dilution rates, see Experimental in the main report), the total ozone production for this formaldehyde addition experiment is shown in Figure 6. When dilution corrected measurements are evaluated, the ozone peak production becomes more substantial (347 ppb). Figure 7 displays the dilution corrected FTIR data for a DE + Toluene summer 2005 experiment. The PAN and ozone production for this experiment are temporally correlated (as often observed in the ambient atmosphere), with a peak PAN mixing ratio (~ 35 ppb) in a range often observed downwind of major urban areas (Grosjean et al 1993; Kleindienst 1994). Figures 8 through 10 show the temporal evolution of selected gas-phase constituents for two DE + Toluene (one replicate), and one DE + OH + VOC summer 2006 experiments. Formic acid is one of the major organic acids found in the atmosphere and may constitute a large fraction of the gas- and aqueous-phase acidity (Finlayson Pitts and Pitts 2000). It is interesting to note that the Ld06sT_1 experimental (06-06-06) results display a higher production of formic acid relative to the replicate (06-09-06, Ld06sT_2), which exceeds the nitric acid (HNO₃) production (Ld06sT_2 does not). While formic acid has been attributed to direct emissions (Grosjean 1992), it appears to be a secondary product throughout these experiments (Nolte et al, 1997). Nitration of particle-phase PAH by HNO₃ has been addressed in past work (Ramdahl et al 1984), but the implications of overall gas- and particle-phase acidity on complex mixture transformation are not well understood.

SOA production appears to be significant for all the light + toluene experiments (Table 7). The dilution corrected mass concentration for Ld06sT_2 in figure 11 (06-09-06) displays a peak PM concentration (60 ug/m³) at 15:30 hr, which represents a significant SOA production capability within the 5.5 hour aging duration (wall losses are not accounted for in this data). Recently it has been postulated that diesel emission associated SOA is routinely underestimated (Robinson et al 2007). It appears that SOA production was more significant in the summer 2005 campaign (versus 2006), and the impact on OC/EC is clearly represented (see time-integrated results below).

1.1.2.2 Time-Integrated data

Organic/Elemental Carbon and Inorganic Ions

Table 9 shows the total OC, EC, total carbon (TC), sulfates and nitrates, whereas detailed data, including all OC and EC fractions are provided in an electronic form as an Appendix F and are available from the HEI website.

Figures 12 show the OC and EC fractions (in $\mu\text{g}/\text{mg}$ of PM mass) and OC/EC ratios, respectively, for these samples. The first three bars represent diesel exhaust aged in the sunlight samples without (L05s_2) and with NO_x denuder (Ld05s_1 and _2, and Ld06s_1). Samples collected in summer 2005 from diesel exhaust + toluene light exposures (Ld05sT_1 and _2) show the highest OC/EC ratio which is consistent with significant amount of SOA formation observed in these experiments. These two samples also show significant POC carbon fraction, indicating formation of highly polar and/or oligomeric products.

It is interesting to note that the two analogues toluene experiments carried out in summer 2006 do not show such high OC/EC ratio or significant POC fraction. However, the Toluene/NO_x ratio was very different in 2005 and 2006 experiments: it was 4 – 5 for 2005 exposures and close to 20 for 2006 exposures. Recent literature have described the dependence of SOA formation from a variety of precursors on NO_x concentrations (e.g., Song et al, 2005; Kroll et al 2006; Pathak et al, 2007), possibly due to the formation of different condensable products under different NO_x conditions.

It can also be seen from Table 9 that the sum of species (i.e. OC+EC+sulfates and nitrates) is much lower for exposures with toluene than for all other light exposures. Since the data are shown for organic carbon (OC), and not organic mass (OM), this indicates that the secondary organic species formed in these exposures are highly oxygenated and/or nitrogenated and the OM/OC ratio is high, most likely in the range of 3 to 4.

Polycyclic Aromatic Hydrocarbons (PAH)

Figure 13 shows the distribution of low mw PAH (LPAH), semi-volatile (SVPAH) and particle (PPAH) PAH in all light exposures. Note that naphthalene was added (2.95 mg, see Table 4 in the main report) to Ld06sV_1 and Ld06sFV_1 exposures. Although most of this PAH reacted during the course of these exposures, especially during the OH radical exposure (Ld06sFV_1), a significant breakthrough the XAD diffusion denuder section is observed (i.e. artificially high naphthalene concentration in the particle phase). The concentrations of PPAH are very low, especially for summer 2006 exposures. Table 10 shows the concentrations of LPAH, SVPAH and PPAH for all light exposures (in $\mu\text{g}/\text{mg}$ EC) and the EC mass measured from the filter.

Nitro-PAH

Figure 14 shows nitro-PAH distribution in all light exposures (in ng/mg EC). The detailed data are provided in Appendix F, available from the HEI web site. In general, the nitro-PAH concentrations are low, below 1 $\mu\text{g}/\text{mg}$ EC, with exception of the runs when naphthalene was added to the chamber (Ld06sV_1 and Ld06FV_1). The most abundant

nitro-PAH is usually 1NN, followed by 2NN, which are distributed between the gas- and particle- phase. This indicates atmospheric formation of both nitronaphthalene isomers. The main report discusses the nitro-PAH data in greater details.

Alkanes Light Exposures

Only samples from the summer 2005 and 2006 campaigns were analyzed for alkanes. Figure 15 shows n-alkanes (from n-tetradecane, nC14 to n-tetracontane, nC40, upper panel), n-alkane-cyclohexanes (from n-heptylcyclohexane, cC13 to nonadecylcyclohexane, cC25, middle panel) and iso-alkanes (norfarnesane, iC14, farnesane, iC15, norpristane, iC18, pristane, iC19 and phytane, iC20, lower panel) in summer 2005 and 2006 dark exposures (in microgram per mg of EC). In general, light exposures show much lower concentrations of n-alkylcyclohexanes and iso-alkanes than dark exposure, most probably due to the reactions of these species with OH radicals.

1.1.3 Chamber and Field Blanks

As explained in Section 3.5.2 of the main report, blank chamber samples were collected in summers 2005 and 2006 prior to the beginning of chamber exposure experiments. One dark chamber blank (D05s) and three light chamber blanks (L05s_1, L06s_1 and L06s_2) were collected. In addition, blanks from XAD-coated denuder section (XAD Den) were obtained before beginning of each campaign (on-site) and filter and XAD cartridge field blanks were also analyzed. Note that all organic speciation data were corrected for the field blanks (i.e. according to the media), but not for chamber blanks.

Figures 16 through 17 show blank data for PAH, nitro-PAH, polar compounds and alkanes. Hopanes and steranes were below detection limit in blanks, so they are not shown. Since the PM mass on blank filters was zero or close to zero, the data are shown in nanograms per sample (ng/sample). The concentrations of individual compounds in blank samples are shown in Appendix G (electronic data base).

Figure 16 A, B and C shows chamber and field blanks for PAH (see Table 6 in the main report for the full compound names). Light PAH (A) and semi-volatile PAH (B) are present in measurable quantities in light chamber blanks in gas (XAD denuder) and particle (XAD+filter) phases. The blanks are not uniform: for example, 9-fluorenone is present in summer 2005 blanks, but not present in 2006 blanks. Particle-phase PAHs are lower in chamber blanks, relative to the XAD cartridge field blank.

Figure 17A shows nitro-PAH in chamber and field blanks (see Table 7 in the main report for the full compound names). The concentrations of nitro-PAH although very low, are above detection limit in these samples. In 2005, the most abundant nitro-PAH in the light chamber blanks was 2-methyl-4-nitronaphthalene (2Me4NN), whereas in 2006 – 4-nitrobiphenyl (4NBip).

Figure 17C shows polar compounds in blanks (see Table 8 in the main report for the full compound names). Only one light chamber blank sample (L06s_2) was analyzed for gas (denuder) and particle (filter+XAD) phase species. In addition, XAD denuder

blank and field filter and XAD cartridge blanks are also shown. It can be seen that the concentrations of polar species are high in the chamber blank, especially for isophthalic (isphac) and succinic (sucac) acids.

Figure 17B shows alkanes in light chamber blank samples (see Table 5 in the main report for the full compound names). The most abundant are gas-phase (XAD denuder) species, including farnesane, tetra-, penta- hexa- and heptadecane.

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Table 1. Initial chamber conditions for all dark exposures carried out in 2005 and 2006

Run Designation	Run Description	NOx Denuder	Injection Duration (min)	Temp (K)	Relative Humidity (mbar)	NO-FTIR (ppb)	NO ₂ -FTIR (ppb)	NO _x -API (ppb)	NO _y -ML (ppb)	N ₂ O ₅ -FTIR (ppb)	O ₃ (ppb)	PM (ug/m ³)	SO ₂ (ppb)
D05w_1	DE	No	3	288.0	0.1478	407	122	523	505	ND	BDL	18.2	1.8
D05w_2 ^a	DE	No	5'	285.2	0.1327	342	175	452	430	ND	BDL	32.4	1.0
	DE	No	3'	285.5	0.2012	845	320	1319	1190	ND	BDL	23.7	3.5
D05w_3	DE	No	2'	286.5	0.2139	558	237	843	768	ND	BDL	27.7	2.5
D05w_4	DE	No	6'	290.6	0.2167	1439	785	O/R	2385	ND	BDL	128.7	9.0
D05w_4	DE	No	6'	289.4	0.2746	1138	1025	O/R	2203	ND	BDL	101.1	6.5
D05wN_5 ^b	DE+NO ₃	No	6'	291.3	0.2158	BDL	944	O/R	2306	1236	2550	101.1	1.5
	DE+NO ₃	No	6'	297.3	0.3032	BDL	1249	O/R	2292	1332	2580	90.5	1.5
D05wN_6 ^c	DE+NO ₃	No	6'	299.6	0.2928	BDL	853	O/R	2554	1108	2575	101.2	1.8
D05wN_2	DE+NO ₃	No	2'	291.2	0.2691	BDL	620	740	774	396	1070	24.4	0.5
D05wN_3	DE+NO ₃	No	2'	285.1	0.1342	13	556	788	798	410	1060	27.5	0.5
D05wN_4	DE+NO ₃	No	3'	283.4	0.1141	ND	529	1053	1091	636	2125	33.3	0.8
Dd05s_1	DE	Yes	9'	299.3	0.2193	553	193	778	704	ND	BDL	15.1	BDL
Dd05s_2	DE	Yes	10'	294.7	0.7106	661	196	965	899	ND	BDL	37.4	ND
Dd05sN_1	DE+NO ₃	Yes	4'	292.6	0.2167	ND	28	49	50	18	1011	11.3	BDL
Dd05sN_2	DE+NO ₃	Yes	3'	289.3	0.1641	ND	42	39	40	17	1022	12.9	BDL
D06s_1	DE	No	6'	295.1	0.47	890	923	1808	1798	ND	BDL	34.5	5.8
D06s_2	DE	No	10'	296.1	0.77	1215	1228	2775	2777	ND	BDL	62.4	7.9
D06s_3	DE	No	10'	299.1	3.74	1102	1021	2676	2635	ND	BDL	66.5	ND
Dd06s_1	DE	Yes	20'	297.5	0.45	ND	9	7	8	ND	1	28.0	BDL
Dd06s_2	DE	Yes	30'	288.4	0.65	ND	15	35	42	ND	BDL	29.2	BDL
Dd06sNV_1	DE+VOC+NO ₃	Yes	28'50"	294.1	0.90	ND	ND	29	35	161	413	33.7	BDL
D06sN_1	DE+NO ₃	No	10'	302.0	2.31	ND	1074	>2000	2369	910	207	67.0	ND

DE=diesel exhaust; ND=No Data. BDL=Below Detection Limit. O/R = Out of Range

a: Samples from 01/15/05 and 01/17/05 were combined for toxicity testing

b: samples from 01/19/05 and 01/20/05 were combined for toxicity testing; c: toxicity sampling only

Table 2. SMPS experimental results for all dark EUPHORE experiments

Name	Run Description	Post-Injection ^a DPM ($\mu\text{g}/\text{m}^3$)	Median ^b diameter (nm)	Mean ^c diameter (nm)	Pre- Sampling ^d DPM ($\mu\text{g}/\text{m}^3$)	Maximum ^e DPM ($\mu\text{g}/\text{m}^3$)	Date
D05w_1	DE	18	44	52	15	20	01/12/05
D05w_2	DE	32	49	55	30	33	01/13/05
D05w_3	DE	29	49	56	22	31	01/14/05
D05w_4	DE	129 ^f and 100 ^g	70 ^f and 57 ^g	75 ^f and 62 ^g	115 ^f and 80 ^g	132 ^f and 112 ^g	01/15/05+ 01/17/05
D05wN_2	DE + NO ₃	25	47	55	15	26	01/24/05
D05wN_3	DE + NO ₃	28	51	55	20	29	01/25/05
D05wN_4	DE + NO ₃	33	52	57	38	40	01/26/05
D05wN_5	DE + NO ₃	104 ^h and 86 ⁱ	63 ^h and 62 ⁱ	67 ^h and 68 ⁱ	59 ^h and 69 ⁱ	111 ^h and 102 ⁱ	01/19/05+ 01/20/05
D05wN_6	DE + NO ₃	96	65	72	76	107	01/21/05
Dd05s_1	DE	15	57	64	14	15	05/10/05
Dd05s_2	DE	37	77	85	21	37	05/25/05
Dd05sN_1	DE + NO ₃	11	67	75	4	11	05/16/05
Dd05sN_2	DE + NO ₃	13	68	77	6	13	05/17/05
D06s_1	DE	35	62	71	7	37	05/25/06
D06s_2	DE	62	61	69	33	66	05/26/06
D06s_3	DE	67	65	74	51	69	06/13/06
Dd06s_1	DE	28	75	84	15	28	05/30/06
Dd06s_2	DE	29	86	94	24	29	05/31/06
Dd06sNV	DE + NO ₃ + VOC	34	91	101	18	34	06/01/06
D06sN	DE + NO ₃	67	58	66	51	68	06/12/06

DE=diesel exhaust; N/A = not applicable, ^a = diesel particulate matter following final injection, ^b = Median particle diameter following final injection, ^c = Mean particle diameter following final injection, ^d = diesel particulate matter immediately before chemistry and toxicity sample collection, ^e = Maximum diesel particulate matter through out entire experiment, ^f = values for 01/15/05, ^g = values for 01/17/05, ^h = values for 01/19/05, ⁱ = values for 01/20/05. All values taken from SMPS total particle volume data assuming $1\text{g}/\text{cm}^3$ density.

Table 3. Experimental results for all dark EUPHORE experiments

Name	Run Description	PAN ^a Max. (ppb)	HONO Max. (ppb)	HCHO ^d Max, Mean, Median (ppb)	Date
D05wN_2	DE + NO ₃	2	35 ^b	ND	01/24/05
D05wN_3	DE + NO ₃	1	31 ^b	ND	01/25/05
D05wN_4	DE + NO ₃	2	32 ^b	ND	01/26/05
D05wN_5	DE + NO ₃	ND	103	ND	01/19/05
	DE + NO ₃	3.5	174 ^b	ND	01/20/05
D05wN_6	DE + NO ₃	1.5	159 ^b	ND	01/21/05
Dd05s_1	DE	ND	5.5 ^c	0.5	05/10/05
Dd05s_2	DE	ND	25 ^c	0.9, 0.3, 0.2	05/25/05
Dd05sN_1	DE + NO ₃	ND	0.7 ^c	2.9, 1.4, 1.2	05/16/05
Dd05sN_2	DE + NO ₃	ND	0.4 ^c	2.3, 1.0, 0.9	05/17/05
D06s_1	DE	ND	50 ^b	ND	05/25/06
D06s_2	DE	ND	78 ^b	2.5	05/26/06
D06s_3	DE	ND	36 ^b	ND	06/13/06
Dd06s_1	DE	ND	ND	3.0	05/30/06
Dd06sNV	DE+NO ₃ +VOC	2.5	ND	3.0	06/01/06
D06sN	DE + NO ₃	3.5	ND	5.0	06/12/06

^a = Measured by GC-ECD ^b = Measured by FTIR, ^c = Measured by LOPAP03, ^d = Measured by AL4021, ND= No Data Available.;
DE=diesel exhaust

Table 4. Carbon and ion data for dark exposures

Name	Filter Mass (mg)	OC (µg/mg)	EC (µg/mg)	TC (µg/mg)	OC/EC	NO3 (µg/mg)	SO4 (µg/mg)	SUM (µg/mg)
D05w_1	0.17	903.01	530.72	1433.73	1.70	9.46	22.02	1465.22
D05w_2	0.36	670.28	242.22	912.50	2.77	7.66	9.82	929.98
D05w_3	0.31	707.67	260.38	968.05	2.72	12.84	10.52	991.41
D05w_4	0.54	783.76	86.90	870.85	9.02	7.47	5.92	884.05
D05wN_2	0.22	451.16	166.51	617.67	2.71	116.20	14.57	748.44
D05wN_4	0.51	497.06	124.85	621.92	3.98	61.94	7.28	691.14
Dd05s_1	0.11	224.91	207.06	431.97	1.09	52.54	23.14	507.65
Dd05s_2	0.08	103.95	196.42	300.37	0.53	146.42	38.32	485.11
Dd05sN_1	0.08	235.82	139.49	375.31	1.69	204.74	106.16	686.21
Dd05sN_2	0.07	279.44	269.31	548.90	1.04	179.71	81.06	809.52
D06s_2	0.39	178.23	234.56	412.79	0.76	49.57	14.39	476.74
D06s_3	0.43	137.99	240.88	378.88	0.57	27.62	4.48	410.97
Dd06s_2	0.28	113.23	214.57	327.79	0.53	24.10	9.76	361.66
Dd06sNV	0.22	133.36	152.49	285.85	0.87	47.20	9.33	342.37
D06sN	0.60	167.23	193.88	361.11	0.86	68.59	5.00	434.70

SUM = sum of species, TC plus sulfates and nitrates

Table 5. Concentrations (in µg/mg of EC) of LPAH, SVPAH and PPAH in all dark exposures

Sample Name	EC (mg)	Sum LPAH	Sum SVPAH	Sum PPAH
Gas Phase				
D05w	n/a	16.91	2.76	0.08
D05wN	n/a	26.72	4.00	0.02
Dd05s_1+2	n/a	12.71	2.51	0.00
Dd05sN_1+2	n/a	3.06	3.03	0.00
D06s	n/a	30.38	5.25	0.00
Dd06s	n/a	25.78	10.72	0.03
D06sN	n/a	2.84	0.40	0.00
Dd06sNV	n/a	124.40	1.83	0.02
Particle Phase				
D05w	0.445	61.77	5.36	0.37
D05wN	0.15	38.98	24.67	1.36
Dd05s_1+2	0.22	3.75	5.75	0.36
Dd05sN_1+2	0.07	14.20	11.26	0.20
D06s	0.155	251.71	1.77	0.15
Dd06s	0.06	120.96	1.58	0.10
D06sN	0.28	40.21	0.76	0.00
Dd06sNV	0.06	759.95	0.30	0.03

LPAH: low molecular weight PAH, mostly gas phase

SVPAH: semi-volatile PAH

PPAH: particle associated PAH

Table 6. Initial chamber conditions for all light exposures carried out in 2005 and 2006.

Run Designation	Run Description	NO _x Denuder	Injection Duration	T (K)	RH (mbar)	NO-FTIR (ppb)	NO ₂ -FTIR (ppb)	NO _x -API (ppb)	NO _y -ML (ppb)	O ₃ (ppb)	PM (ug/m ³)	SO ₂ (ppb)
L05s_1	CB	No	0	291.4	0.1999	BDL	BDL	3	3	BDL	<1	BDL
Ld05s_1	DE	Yes	6'	294.3	0.1461	187	50	208	195	BDL	9.6	BDL
Ld05s_2	DE+Sun	Yes	4'	292.7	0.2353	52	22	84	83	BDL	11.3	BDL
Ld05sF_1	DE+Sun+OH	Yes	3'	292.5	0.2081	73	65	109	110	BDL	8.4	BDL
Ld05sF_2	DE+Sun+OH	Yes	4'	291.1	0.2048	ND	80	152	149	BDL	14.7	BDL
Ld05sF_3	DE+Sun+OH	Yes	3'45"	293.3	0.1516	185	75	264	253	BDL	16.1	BDL
Ld05sF_4	DE+Sun+OH	Yes	2'44"	293.0	0.1882	74	77	138	135	BDL	10.4	BDL
Ld05sT_1	DE+Sun+Toluene	Yes	3'30"	290.0	0.1789	ND	128	148	139	BDL	8.9	BDL
Ld05sT_2	DE+Sun+Toluene	Yes	4'15"	291.9	0.2325	ND	81	110	103	BDL	11.6	BDL
L05s_2	DE+Sun	No	10'	292.2	0.3652	864	845	1844	1693	2	37.1	ND
L06s_1	CB	No	0	295.6	1.73	ND	ND	3	4	1	<1	2.1
L06s_2	CB	No	0	292.8	1.96	ND	ND	5	5	25	<1	0.7
Ld06sV_1	DE+Sun+VOC	Yes	27'12"	295.9	0.62	ND	ND	66	64	4	53.8	BDL
Ld06s_1	DE+Sun	Yes	30'	297.4	1.58	ND	ND	27	28	1	41.8	BDL
Ld06sF_1	DE+Sun+OH	Yes	37'	298.2	0.75	ND	ND	27	27	BDL	36.1	BDL
Ld06sFV_1	DE+Sun+OH+VOC	Yes	30'	297.6	1.42	ND	ND	25	27	BDL	29.5	BDL
Ld06sT_1	DE+Sun+Toluene	Yes	35'	298.0	0.93	ND	ND	24	25	BDL	31.3	BDL
Ld06sT_2	DE+Sun+Toluene	Yes	10'	295.5	1.66	ND	ND	30	33	BDL	38.9	BDL

CB=chamber blank; DE=diesel exhaust; BDL= below detection limit; ND= not determined;

Table 7. SMPS experimental results for all EUPHORE light experiments

Name	Run Description	Post-Injection ^a DPM ($\mu\text{g}/\text{m}^3$)	Median ^b diameter (nm)	Mean ^c diameter (nm)	Pre- Sampling ^d DPM ($\mu\text{g}/\text{m}^3$)	Maximum ^e DPM ($\mu\text{g}/\text{m}^3$)	Date
L05s_1	CB	N/A	<50	<50	<1 ^j	<1 ^j	05/09/05
Ld05s_1	DE+Sun	10	60	67	4	10	05/11/05
Ld05s_2	DE+Sun	11	69	76	4	11	05/12/05
Ld05sF_1	DE+Sun+OH	8	68	76	3	8	05/13/05
Ld05sF_2	DE+Sun+OH	15	70	79	6	15	05/18/05
Ld05sF_3	DE+Sun+OH	16	70	80	7	16	05/23/05
Ld05sF_4	DE+Sun+OH	10	69	78	5	10	05/24/05
Ld05sT_1	DE+Toluene	9	69	77	54	57	05/19/05
Ld05sT_2	DE+Toluene	11	68	76	61	63	05/20/05
L05s_2	DE+Sun	37	77	85	7	37	05/26/05
L06s_1	CB	N/A	<50	<50	<1 ^j	1	05/23/06
L06s_2	CB	N/A	<50	<50	<1 ^j	<1 ^j	05/24/06
Ld06sV_1	DE+Sun+VOC	54	88	100	26	55	06/02/06
Ld06s_1	DE+Sun	42	94	103	24	42	06/08/06
Ld06sF_1	DE+Sun+OH	36	89	99	21	37	06/05/06
Ld06sFV_1	DE+Sun+OH+VOC	30	91	100	19	32	06/07/06
Ld06sT_1	DE+Toluene	31	87	96	36	41	06/06/06
Ld06sT_2	DE+Toluene	39	93	102	53	54	06/09/06

CB=chamber blank; N/A = not applicable, ^a = diesel particulate matter following final injection, ^b = Median particle diameter following final injection, ^c = Mean particle diameter following final injection, ^d = diesel particulate matter immediately before chemistry and toxicity sample collection, ^e = Maximum diesel particulate matter through out entire experiment, ^j = values approaching instrument detection limit. All values taken from SMPS particle volume data assuming $1\text{g}/\text{cm}^3$ density. All values are *in-situ* and have not been corrected for dilution or wall loss.

Table 8. Experimental results for all EUPHORE light experiments

Name	Run Description	PAN Max. (ppb)	HONO ^c Max. (ppb)	HCHO Max, Mean, Median (ppb)	Ozone ^e Max. (ppb)	Date
L05s_1	CB	ND	ND	6.9 ^d 2.9 ^d 2.2 ^d	22.4	05/09/05
Ld05s_1	DE+Sun	ND	1.5	8.5 ^d 3.1 ^d 2.3 ^d 9 ^b 5 ^b 5 ^b	6.8	05/11/05
Ld05s_2	DE+Sun	ND	0.8	4.2 ^d 2.5 ^d 2.6 ^d	11.0	05/12/05
Ld05sF_1	DE+Sun+OH	ND	1.9	135.3 ^d 15.6 ^d 4.2 ^d 139 ^b 38 ^b 25 ^b	59.4	05/13/05
Ld05sF_2	DE+Sun+OH	ND	3.0	OR ^d 26.8 ^d 10.2 ^d 298 ^b 43 ^b 16 ^b	149	05/18/05
Ld05sF_3	DE+Sun+OH	ND	5.9	382 ^b 94 ^b 49 ^b	106	05/23/05
Ld05sF_4	DE+Sun+OH	ND	2.9	403 ^b 60 ^b 18 ^b	223	05/24/05
Ld05sT_1	DE+Toluene	28 ^b	4.4	51.5 ^d 20.1 ^d 14.6 ^d 41 ^b 22 ^b 21 ^b	286	05/19/05
Ld05sT_2	DE+Toluene	14 ^b	4.4	51.0 ^d 16.4 ^d 10.0 ^d 48 ^b 25 ^b 27 ^b	251	05/20/05
L05s_2	DE+Sun	ND	14.0	5.4 ^d 3.5 ^d 3.8 ^d 8 ^b 4 ^b 4 ^b	2.9	05/26/05
L06s_1	CB	ND	ND		5	05/23/06
L06s_2	CB	2 ^a	ND	11 ^b 6 ^b 7 ^b	51	05/24/06
Ld06sV_1	DE+Sun+VOC	23 ^a	ND	30 ^d	188	06/02/06
Ld06s_1	DE+Sun	ND	ND	ND	20	06/08/06
Ld06sF_1	DE+Sun+OH	5 ^a	ND	252 ^b 37 ^b 13 ^b	145	06/05/06
Ld06sFV_1	DE+Sun+OH+VOC	19 ^a	ND	263 ^b 58 ^b 32 ^b	251	06/07/06
Ld06sT_1	DE+Toluene	14 ^a	ND	37 ^b 13 ^b 10 ^b	112	06/06/06
Ld06sT_2	DE+Toluene	>10 ^{a,f}	ND	20 ^b 10 ^b 10 ^b	184	06/09/06

^a= Measured by GC-ECD ^b= Measured by FTIR, ^c= Measured by LOPAP03, ^d= Measured by AL4021, ^e= Measured by O₃-ML9810-SN2028, ^f= data incomplete, highest value recorded instrument malfunction, CB=chamber blank; BDL= Below Detection Limit, ND= No Data Available, OR = Out of Range

Table 9. Carbon and ion data for light exposures

Name	Filter Mass (mg)	OC (µg/mg)	EC (µg/mg)	TC (µg/mg)	OC/EC	NO3 (µg/mg)	SO4 (µg/mg)	SUM (µg/mg)
L05w	0.25	589.07	235.22	824.29	2.50	81.72	19.13	925.13
L05s_2	0.05	233.80	149.90	383.70	1.56	230.18	53.28	667.16
Ld05s_1	0.08	313.19	196.74	509.92	1.59	98.33	28.12	636.37
Ld05s_2	0.08	232.96	156.01	388.97	1.49	103.92	28.80	521.69
Ld05sF_1	0.03	471.79	224.45	696.55	2.10	354.17	152.79	1203.51
Ld05sF_2	0.11	241.39	162.39	403.78	1.49	125.66	48.95	578.38
Ld05sF_3	0.11	203.33	152.48	355.81	1.33	133.14	42.78	531.73
Ld05sT_1	0.76	204.50	30.72	235.22	6.66	17.57	5.31	258.10
Ld05sT_2	0.79	207.29	34.14	241.43	6.07	14.66	4.43	260.52
Ld06s_1	0.14	159.49	276.73	436.22	0.58	29.65	8.49	474.36
Ld06sV_1	0.31	167.46	72.45	239.91	2.31	32.60	7.82	280.33
Ld06sF_1	0.25	176.13	121.20	297.33	1.45	26.36	10.25	333.94
Ld06sFV_1	0.25	179.49	113.26	292.74	1.58	37.39	11.59	341.73
Ld06sT_1	0.44	135.28	78.64	213.92	1.72	18.83	8.36	241.11
Ld06sT_2	0.59	136.19	123.77	259.96	1.10	44.66	6.93	311.55

Table 10 Concentrations (in µg/mg of EC) of LPAH, SVPAH and PPAH in all light exposures

Sample Name	EC (mg)	Sum LPAH	Sum SVPAH	Sum PPAH
Gas Phase				
Ld05s_1+2	n/a	9.11	11.69	0.00
L05s_2	n/a	14.55	11.33	0.00
Ld05sF	n/a	3.69	2.97	0.00
Ld05sT	n/a	8.94	18.93	0.00
Ld06sV_1	n/a	41.26	4.17	0.00
Ld06s_1	n/a	13.70	0.47	0.00
Ld06sF_1	n/a	14.52	1.80	0.00
Ld06sFV_1	n/a	44.35	28.90	0.00
Ld06sT	n/a	15.04	0.40	0.00
Particle Phase				
L05s_2	0.14	10.94	15.49	0.33
Ld05s_1+2	0.08	8.17	5.46	0.19
Ld05sF	0.135	4.80	9.48	0.35
Ld05sT	0.06	9.23	8.89	0.27
Ld06sV_1	0.07	754.27	2.31	0.11
Ld06s_1	0.07	33.97	4.33	0.01
Ld06sF_1	0.05	3.64	3.70	0.00
Ld06sFV_1	0.02	80.85	1.75	0.20
Ld06sT	0.035	37.57	4.43	0.05

LPAH: low molecular weight PAH, mostly gas phase

SVPAH: semi-volatile PAH

PPAH: particle associated PAH

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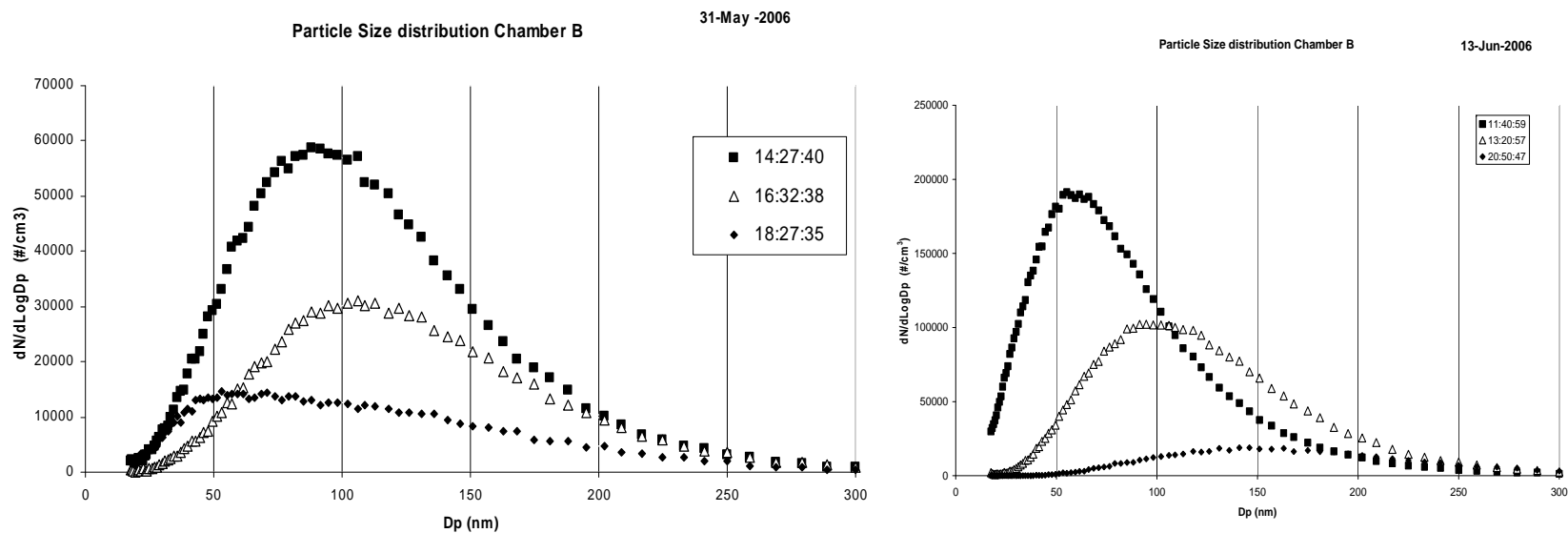


Figure 1. Particle size and number concentration distribution during diesel exhaust aging in EUPHORE chamber in the dark in summer 2006; (A) with NOx denuder (initial DPM concentration 30 $\mu\text{g}/\text{m}^3$); (B) without NOx denuder (initial DPM 65 $\mu\text{g}/\text{m}^3$). The legend indicates particles right after diesel exhaust injection (\blacksquare), after two hours of aging (\blacktriangle) and after 4 hrs of aging (\blacklozenge).

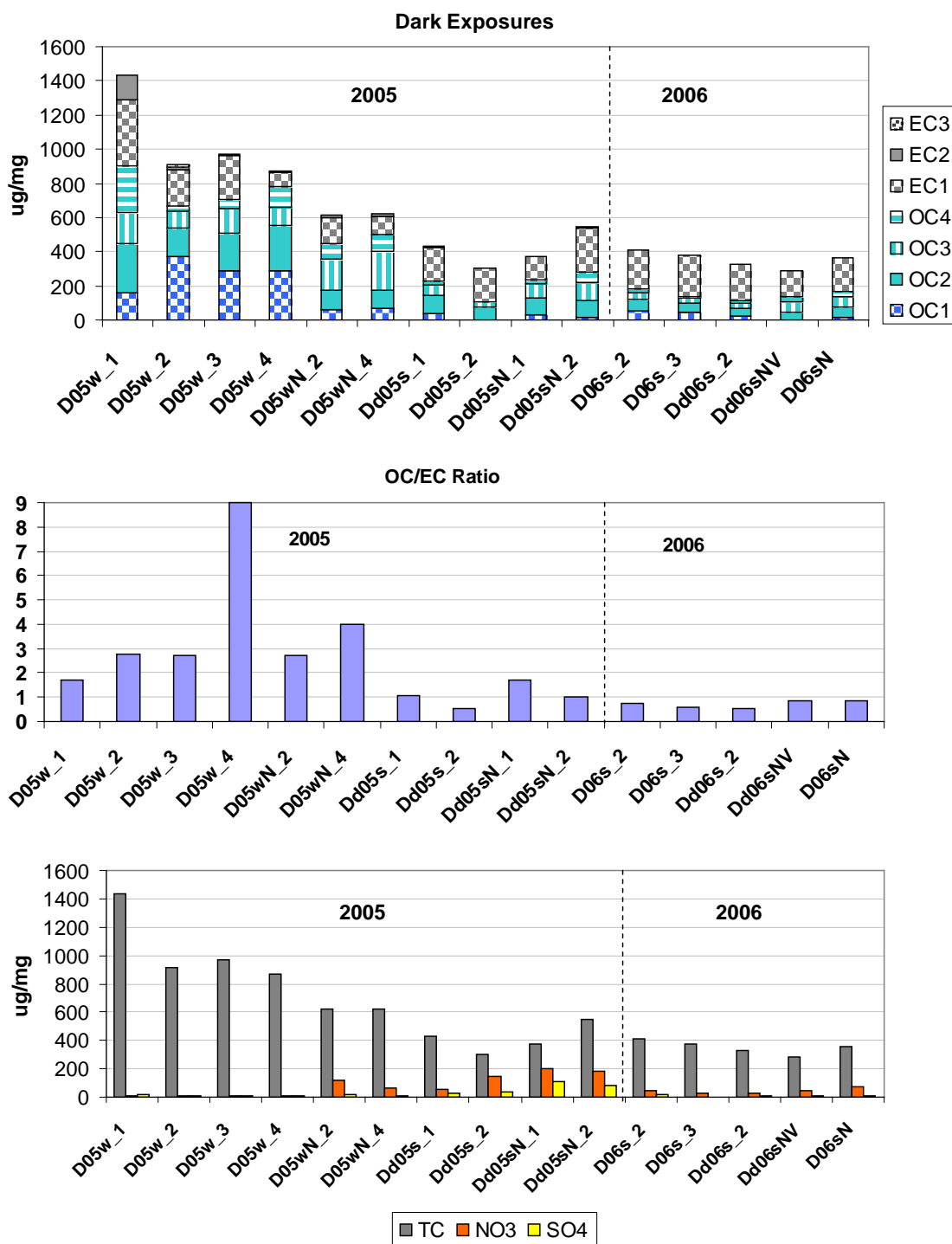


Figure 2. Carbon fractions (upper panel), OC/EC ratios (middle) and total carbon, sulfates and nitrates (bottom) for dark exposures. Sample identification: D=Dark; d=NO_x denuder present; 05 or 06: 2005 or 2006 campaign; s=summer; w = winter; N = added NO₃; V = added VOC

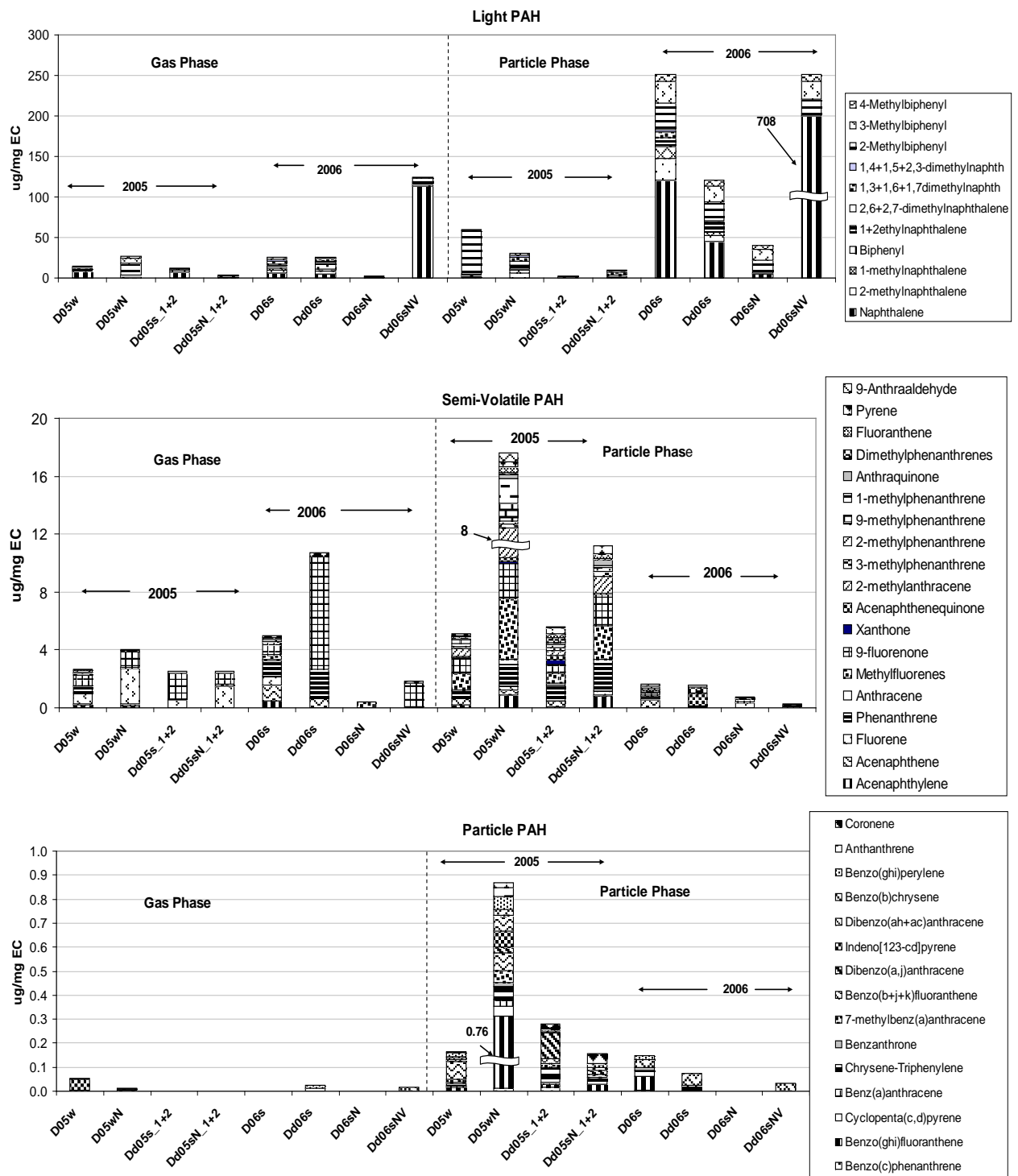


Figure 3. PAH distribution in all dark exposures. Sample identification: D=Dark; d=NO_x denuder present; 05 or 06: 2005 or 2006 campaign; s=summer; w = winter; N = added NO₃; V = added VOC.

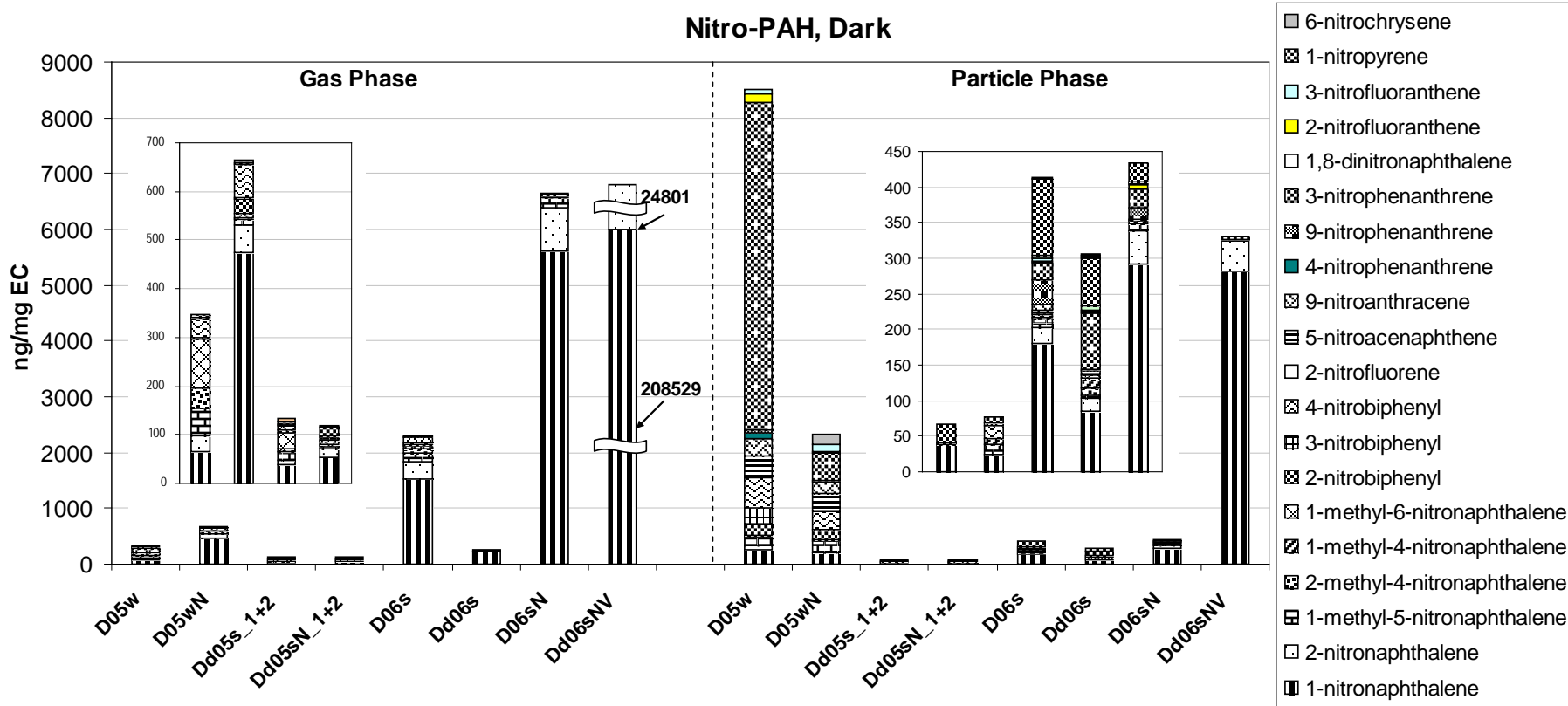


Figure 4. Nitro-PAH in all dark exposure. Sample identification: D=Dark; d=NO_x denuder present; 05 or 06: 2005 or 2006 campaign; s=summer; w = winter; N = added NO₃; V = added VOC

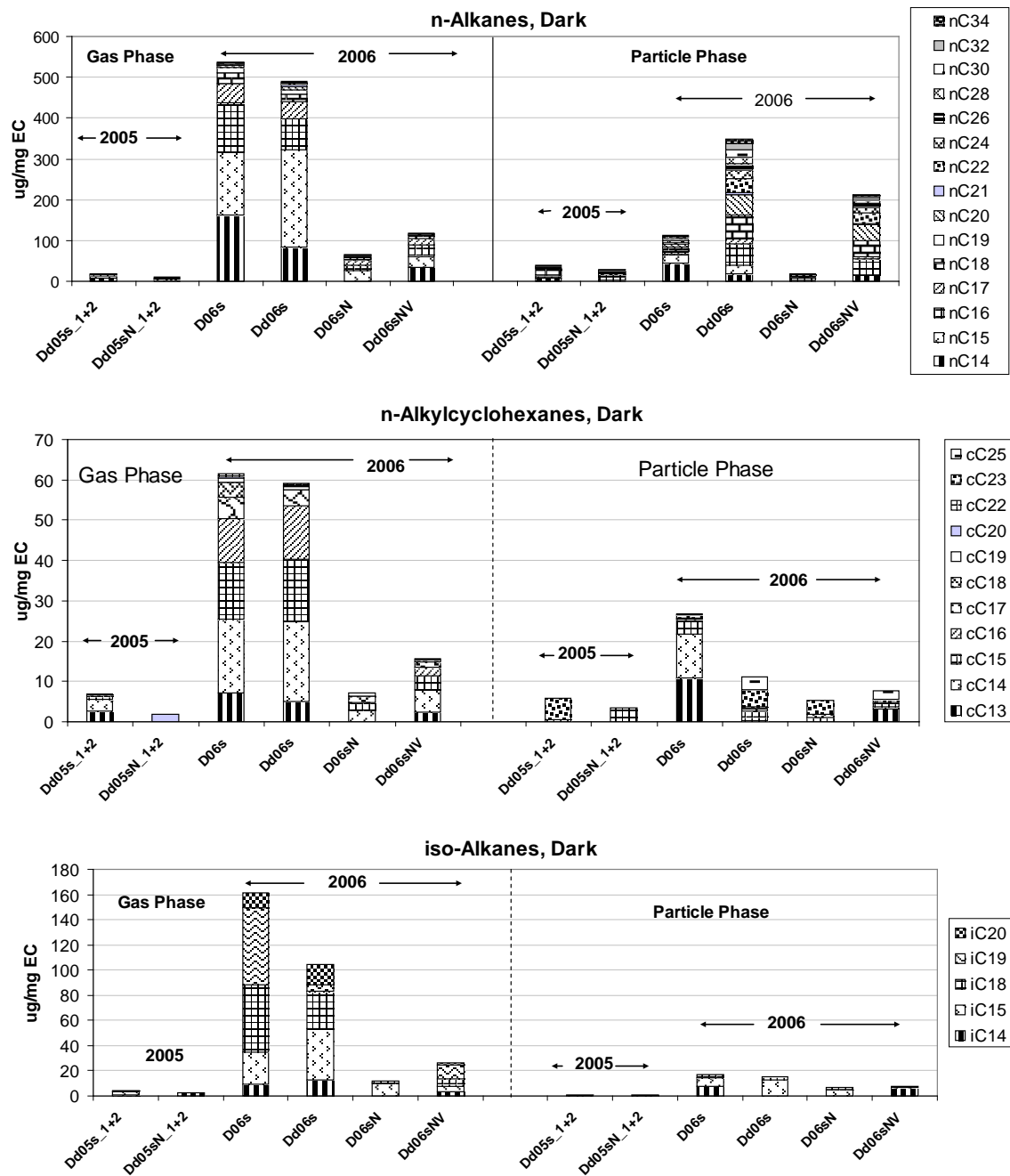


Figure 5. n-Alkanes (upper panel), n-alkyl-cyclohexanes (middle panel) and iso-alkanes in dark exposures. See text for sample description.

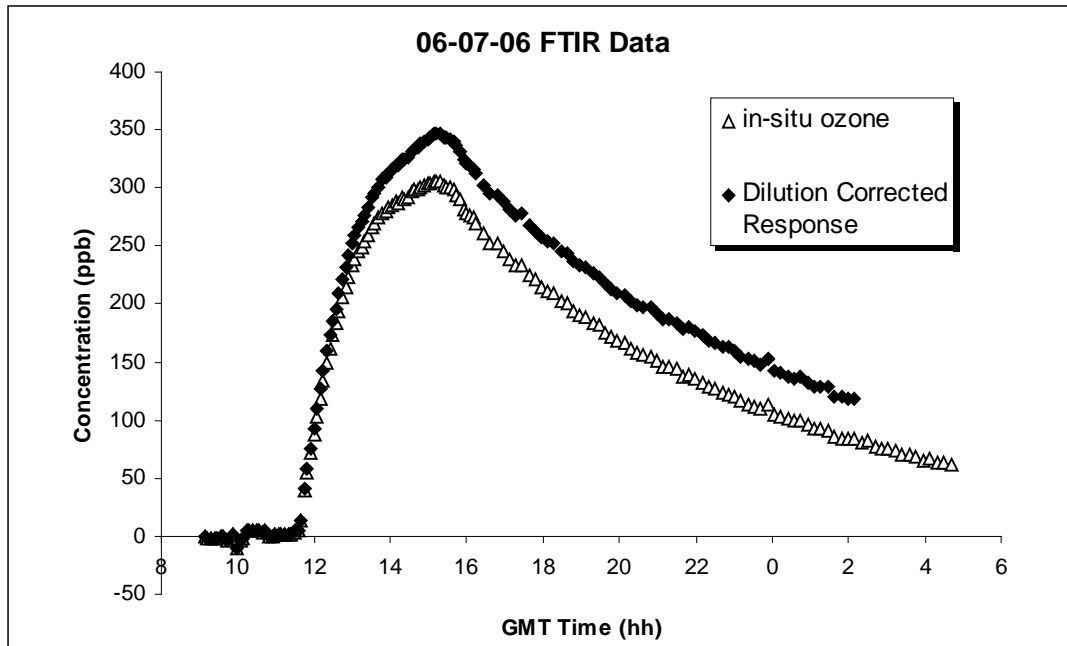


Figure 6. Summer 2006 campaign, DE+OH+VOC (Ld06sFV_1). Shows dilution correction for ozone (peak = 347ppb) versus in-situ (peak = 306) measurements.

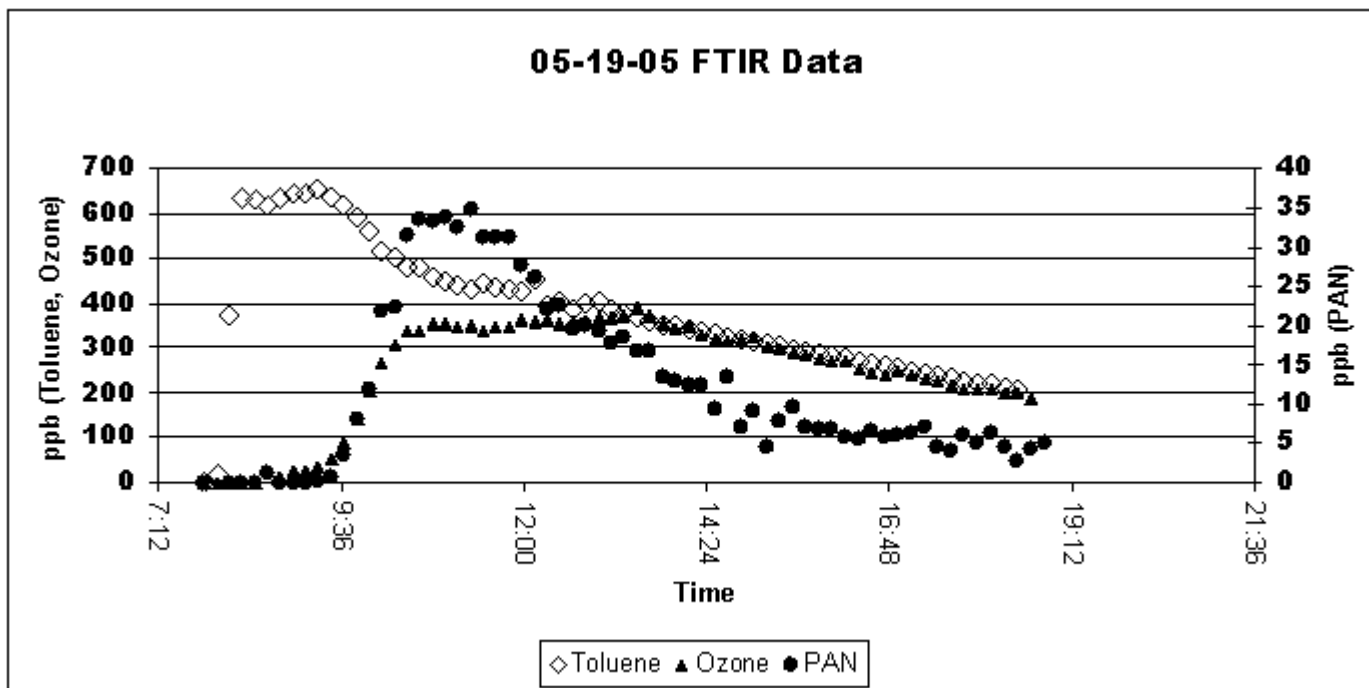


Figure 7. Summer 2005 DE + Toluene (Ld05sT_1) exposure, PAN and ozone production (data corrected for dilution).

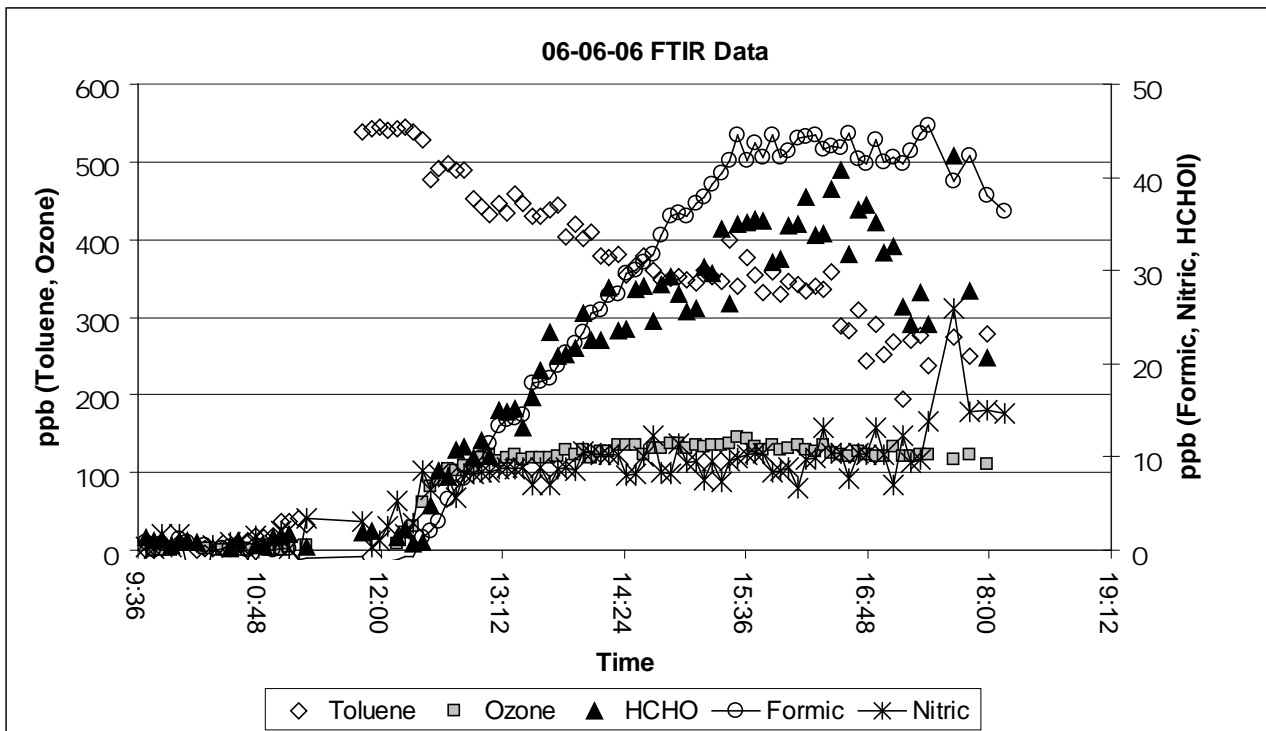


Figure 8. Summer 2006 DE + Toluene (Ld06sT_1). Formic = formic acid; nitric = nitric acid, HCHO = formaldehyde (data corrected for dilution).

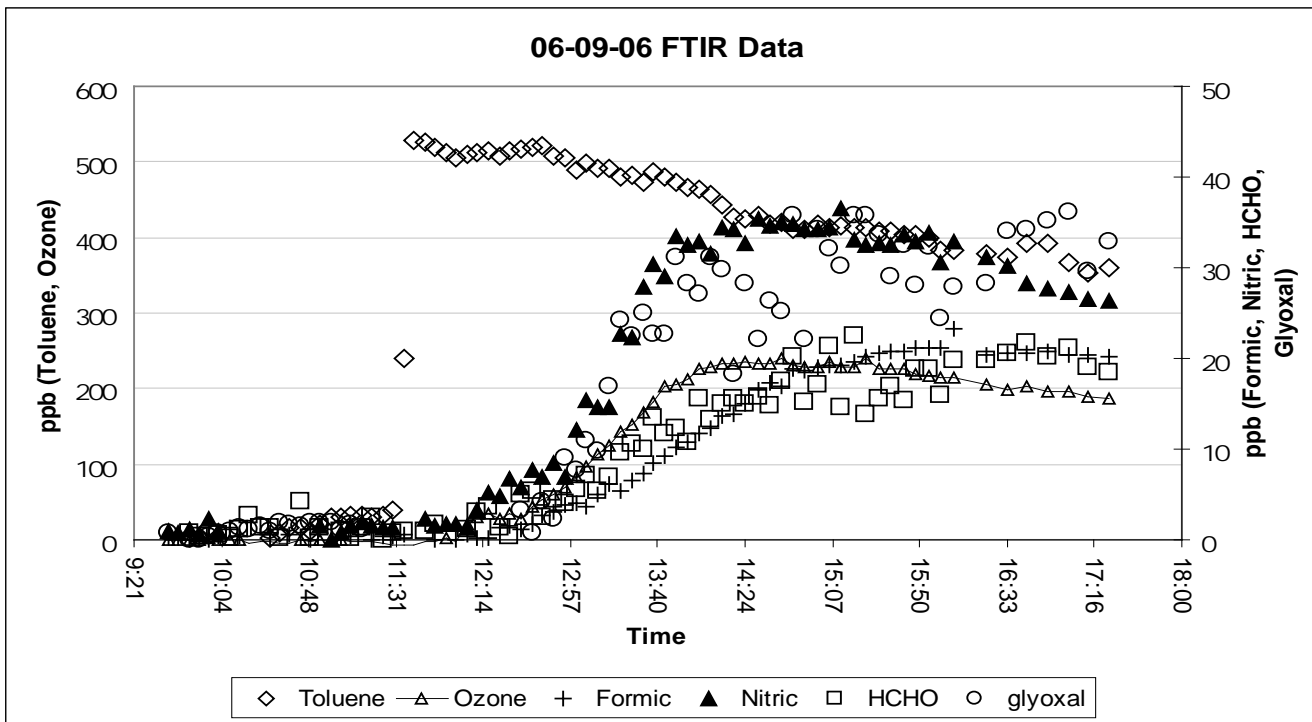


Figure 9. Summer 2006 DE + Toluene Replicate, Ld06sT_2 (data corrected for dilution).

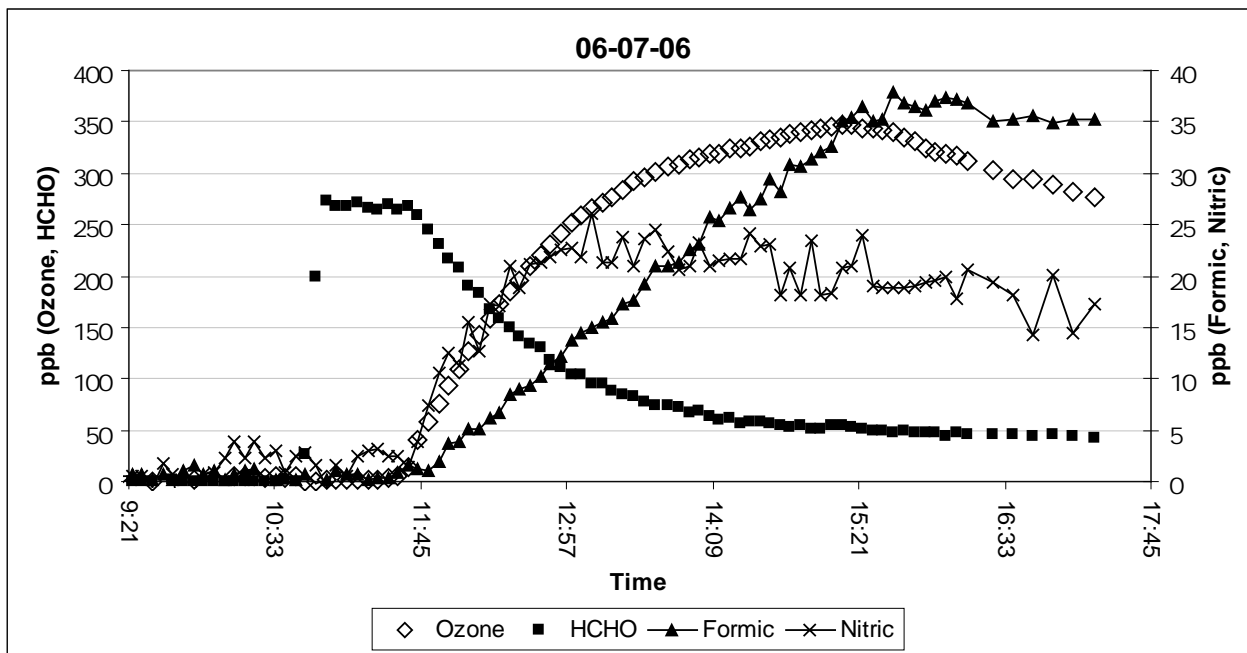


Figure 10. Summer 2006 DE + HCHO + VOC. (Data corrected for dilution).

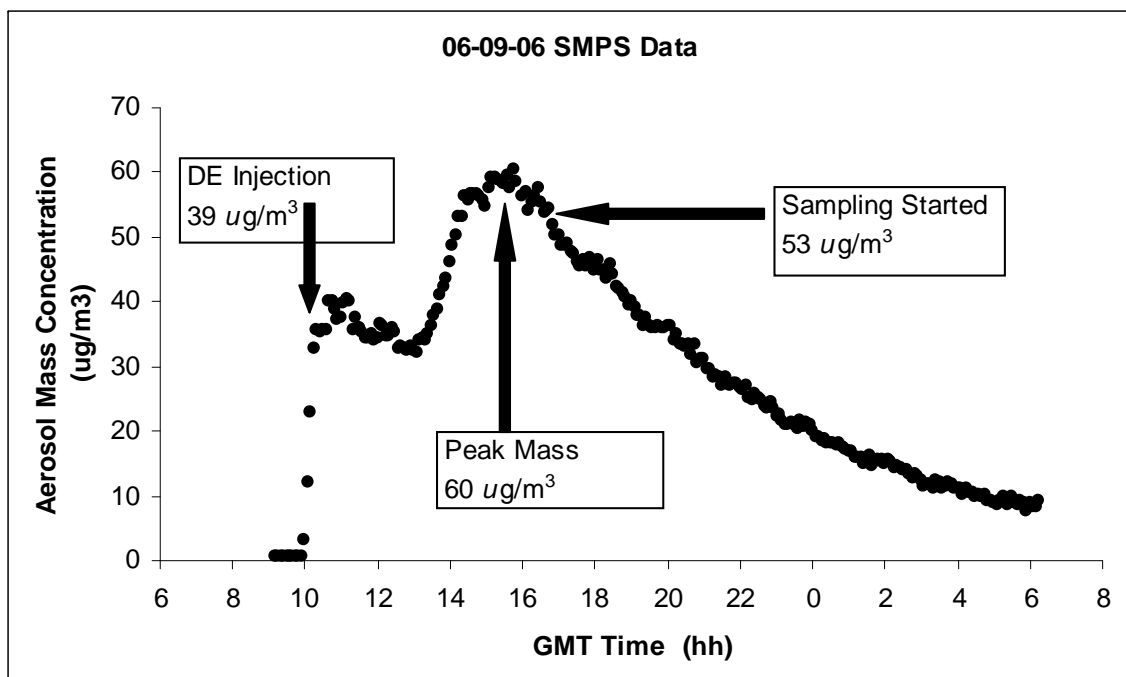


Figure 11. Summer 2006, aerosol mass for a DE + Toluene light experiment (All values taken from SMPS total particle volume data assuming 1g/cm³ density).

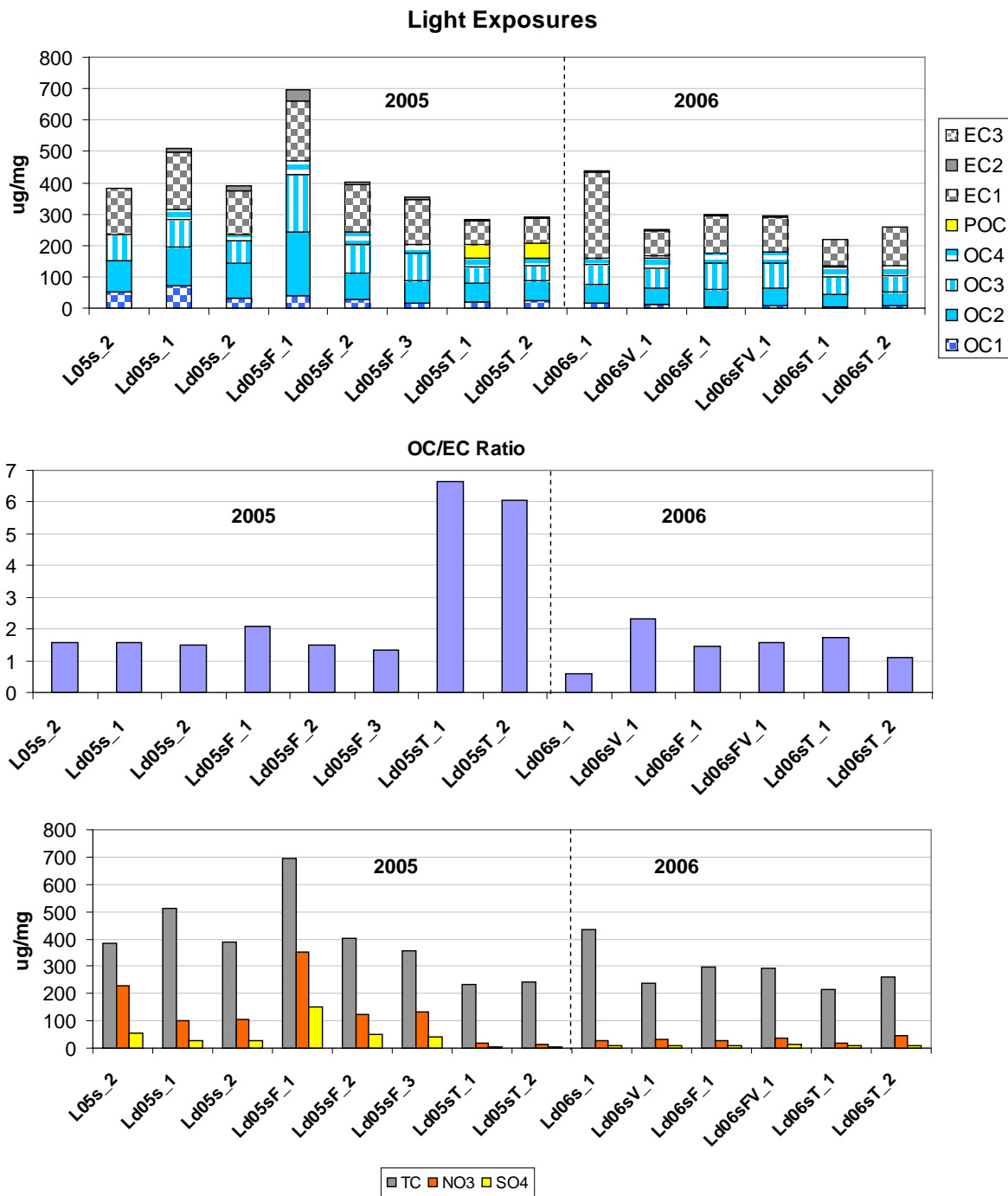


Figure 12. Carbon fractions (upper panel), OC/EC ratios (middle) and total carbon, nitrates and sulfates (bottom) for light exposures. Sample identification: L = Light; d = NO_x denuder present; 05 or 06:=2005 or 2006 campaign; s = summer; V= added VOC; F = added formaldehyde (OH); T = added toluene.

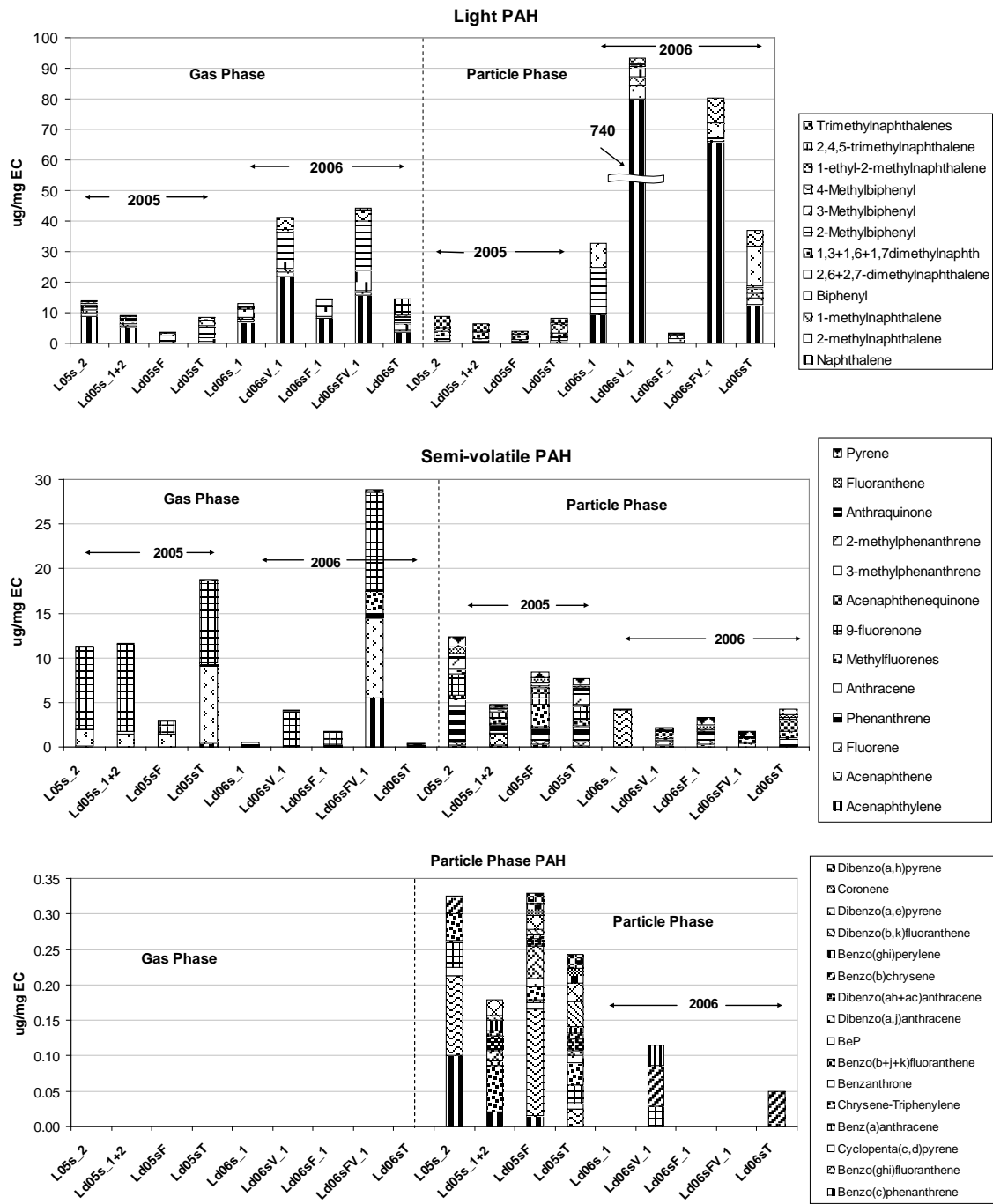


Figure 13. PAH distribution in all light exposures. Upper panel: low mw PAH (LPAH), middle panel: semi-volatile PAH (SVPAH) and bottom panel: particle phase PAH (PPAH) Sample identification: L = Light; d = NO_x denuder present; 05 or 06:=2005 or 2006 campaign; s = summer; V= added VOC; F = added formaldehyde (OH); T = added toluene.

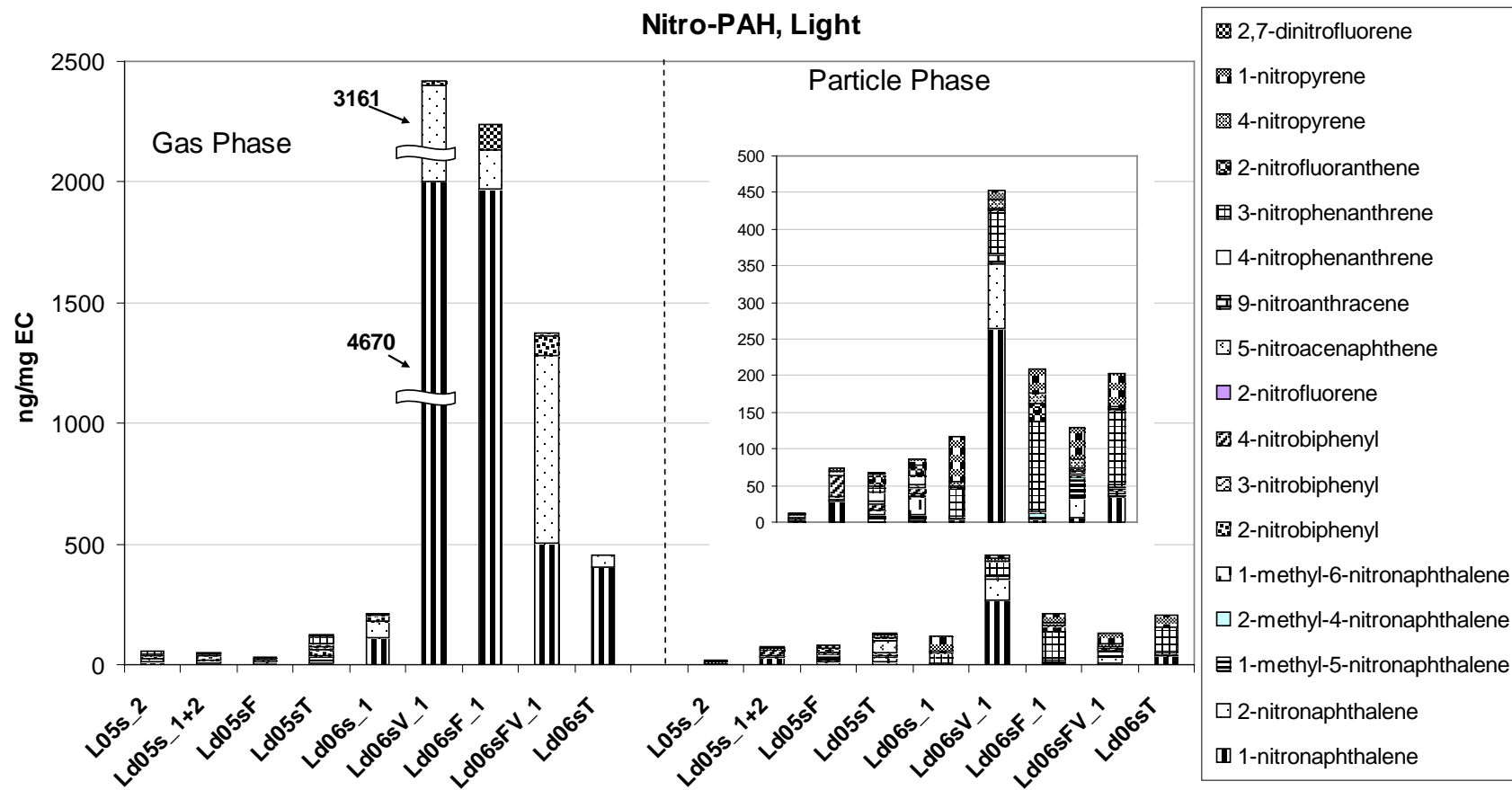


Figure14. Nitro-PAH in all light exposure. Sample identification: L = Light; d = NO_x denuder present; 05 or 06:=2005 or 2006 campaign; s = summer; V= added VOC; F= added formaldehyde (OH); T = added toluene.

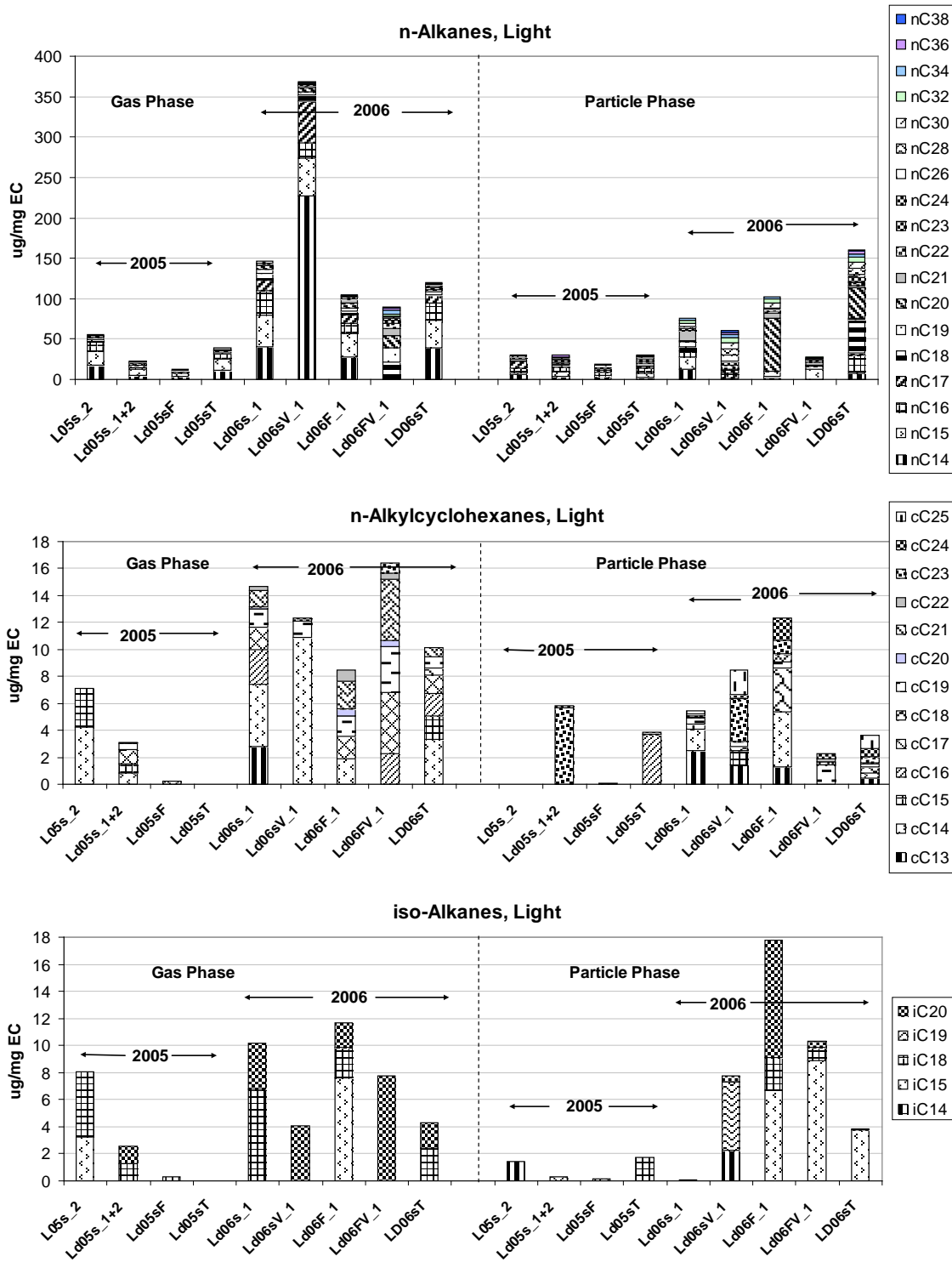


Figure 15. n-Alkanes (upper panel), n-alkyl-cyclohexanes (middle panel) and iso-alkanes in dark exposures. See text for sample description.

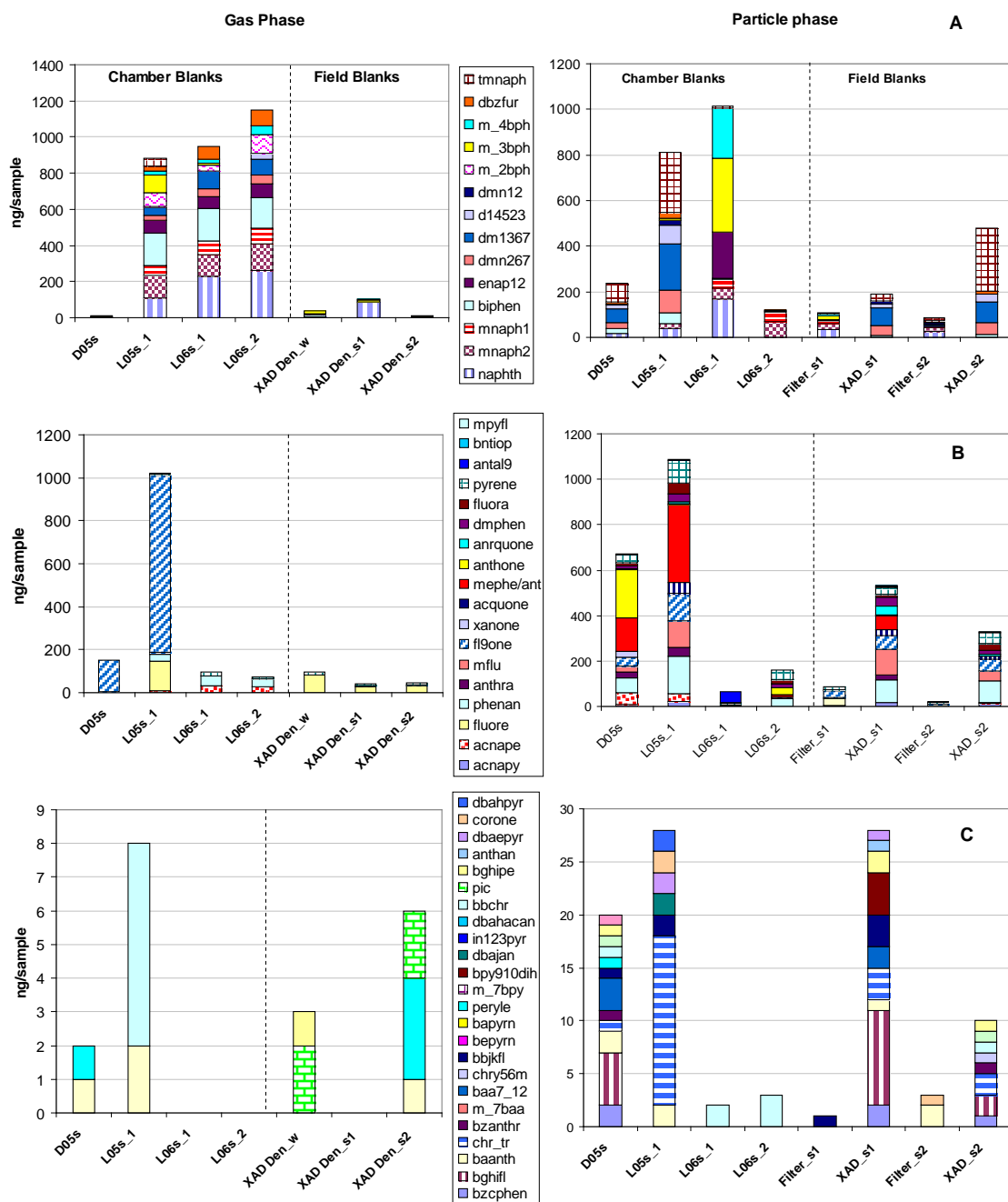


Figure 16. PAH in the chamber and field blank samples Sample identification: L=light, D=dark; 05 or 06= 2005 Or 2006 campaign; s=summer; w=winter, XAD Den =XAD denuder blank; Filter=filter blank; XAD=XAD cartridge blank

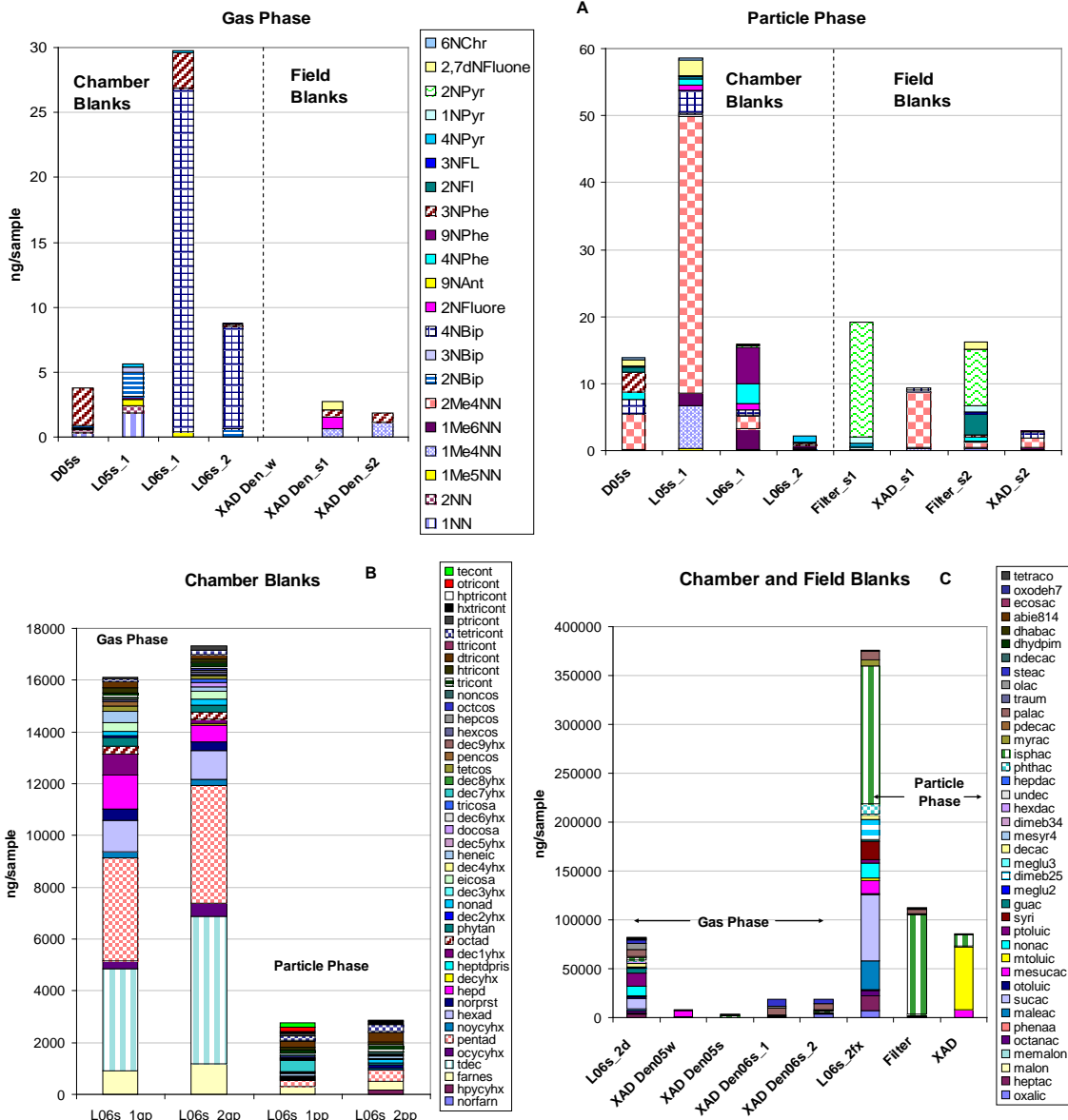


Figure 17. Chamber and field blanks for nitro-PAH (A) and polar compounds (C) and chamber blanks for alkanes (B) Sample identification: L=light, D=dark; 05 or 06= 2005 or 2006 campaign; s=summer; w=winter, XAD Den =XAD denuder blank; Filter=filter blank; XAD=XAD cartridge blank.