Appendix B. Correlations and Ratios between Pollutants on an Annual Basis

Note: Appendices Available on the Web appear in a different order than in the original Investigators’ Report. HEI has not changed these documents. Appendices were relettered as follows:

- Appendix B was originally Appendix A
- Appendix C was originally Appendix B
- Appendix D was originally Appendix C
- Appendix E was originally Appendix D

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Appendix A. Correlations and ratios between pollutants on a yearly basis

A.1 Correlations

An inspection of the correlations and ratios between pollutants on a yearly basis provides further insights about the changes of the air pollutant mixtures over the whole study period.

Figure A. 1 shows the spearman correlation coefficients between SO$_2$ and selected pollutants, calculated for each year separately. Whereas at the beginning of the first sub-period strong correlations both with gaseous pollutants as well as with particles were observed, the correlations became weaker in 1995 (which was the year with the strongest decrease of the SO$_2$ levels). During the second sub-period, the correlation coefficients between SO$_2$ and the other pollutants increased significantly and decreased again from 1998 on. This pattern appeared in winter seasons as well as in summer seasons (data not shown).

Figure A. 2a and 2b show the Spearman correlation coefficients between NO and selected pollutants, calculated for each year separately and stratified by season. The correlation coefficients in winter seasons were in general higher and more stable than in summer seasons. However, a slightly decreasing trend could be seen for the correlation between NO and CO. In winter 1995/96 the correlation coefficients between NO and NO$_2$ as well as between NO and PM$_{10}$ were clearly lower than in the adjacent winters. The weak correlation between NO and NO$_2$ in winter 1994/95 was an outlier caused by the implausible NO$_2$ values (from April 1$^{st}$, 1994 to February 1$^{st}$, 1995). The summer trend was less clearly. The correlation coefficients between NO and CO were going down, whereas the correlations between NO and particle mass or number concentrations exhibited a slightly increasing trend. The correlation between NO and NO$_2$ in summer 1994 must be interpreted in sight of the implausible NO$_2$ data as an outlier.

Figure A. 3a and b show the spearman correlation coefficients between CO and selected pollutants, calculated for each year separately and stratified by season. Whereas from summer
1996 on, a decreasing trend was observed for all relationships between CO and other pollutants, they remain rather constant in the winter seasons (except CO vs. SO2, as discussed above). The weak correlation between CO and NO2 in winter 1994/95 \( r=0.13 \) was, similar to the relationship between NO and NO2, caused by the implausible NO2 values in this period and therefore an outlier. The correlation between CO and NO2 calculated only for the remaining months February and March \( n=59 \) was clearly higher \( r=0.86 \).

Figure A. 4a and b show the spearman correlation coefficients between O3 and selected pollutants, calculated for each year separately and stratified by season. The strongest negative correlation was observed between ozone and NO (the coefficients range between -0.7 and -0.9 in the winter seasons, and between -0.4 and -0.7 in the summer seasons, data not shown). The correlations between ozone and the other pollutants were in general stronger in cold seasons. All considered pollutants were in winter negatively correlated with O3. Similar to CO the correlation between O3 and the other pollutants was weaker in the winter season 1995/96. Only the correlation between O3 and CO remained strong during all winter periods. There was nearly no correlation between O3 and SO2 or particulate air pollutants in summer.

Figure A. 5a and b show the spearman correlation coefficients between PM10 and other particulate pollutants; PM2.5, fine and ultrafine particle number concentration. The correlations were calculated for each year separately and stratified by season. A more pronounced pattern was observed for the summer seasons, whereas the correlations remained stable during the winter seasons. The correlations between particle mass and particle number concentrations were striking low in summer seasons (between 0.2 and 0.4). During winter, the correlations between MC and NC were stronger.

**A.2 Ratios between selected air pollutants**

The ratio between selected air pollutants is a further index to characterize the changes of the source structure. The ratios of pollutants are, similar to the correlation coefficients, less
dependent from temporal variation of sources and meteorological conditions when compared with individual concentrations of pollutants. Here is particularly the consideration of the CO/NOx and SO2/NOx relationships important and insightful. Mobile emission sources are predominately characterized by high CO/NOx ratios and low SO2/NOx ratios, while point source emissions are characterized by lower CO/NOx ratios and higher SO2/NOx ratios (Aneja et al. 2001).

In Figure A. 6 the CO/NOx ratios calculated for each year separately and stratified by season are shown. The ratios for summer 1994 and winter 1994/95 couldn’t be calculated due to the implausible NO2 values in those seasons. Both the summer as well as the winter values show decreasing trend in the second sub-period and a light increasing trend in the third sub-period.

The ratios between SO2 and NOx, calculated for each year separately and stratified by season, are shown in the Figure A. 7. Similar to the CO/NOx ratios there is a strong decrease in the second sub-period, but no increase in the third sub-period of the study. The decrease of the SO2/NOx is clearly caused by the drop of SO2 levels during the study period. The changes of the ratios between SO2 and other pollutants have similar pattern (data not shown).

The ratios between NO and NO2 are shown in Figure A. 8. The NO/NO2 ratios are clearly higher in the winter seasons than in the summer seasons (average value in the winter seasons without winter 1993/94 was 0.7 in comparison with 0.4 in the summer seasons). During the second and the third study sub-periods a continuously decrease of the winter ratios was observed, whereas the summer ratios were more stable.

The ratios between the particulate air pollutants are shown in Figure A. 9 and Figure A. 10. The PM2.5 (measured by MAS) / PM10 (measured by HI) ratio is in winter seasons higher than in summer (the average mean estimated for the winter seasons is 0.85 and for the summer seasons 0.65). It means that the coarse fraction of particles (particles between 2.5 and 10 µm) in the PM10 fraction is larger in summer than in winter. A visible increase of the PM2.5/PM10
ratio could be seen for the last two years of the study period 2000 and 2001.

In opposite to the PM$_{2.5}$/PM$_{10}$ ratio the differences between the PM$_{2.5}$/NC$_{2.5}$ in the winter and the summer time are less pronounced (r=0.0020 for the winter and 0.0016 for the summer seasons, respectively). Whereas the ratios decreased during the 90ties, there is an increase from 2000 onwards.
Figure A. 1: Spearman correlation coefficients for the relationship between SO$_2$ and other pollutants by year.

Figure A. 2: Spearman correlation coefficients for the relationship between NO and other pollutants by year and season, a) for summer seasons, b) for winter seasons.

Figure A. 3: Spearman correlation coefficients for the relationship between CO and other pollutants by year and season, a) for summer seasons, b) for winter seasons.

Figure A. 4: Spearman correlation coefficients for the relationship between O$_3$ and other pollutants by year and season, a) for summer seasons, b) for winter seasons.

Figure A. 5: Spearman correlation coefficients for the relationship between PM$_{10}$ and other particulate pollutants by year and season, a) for summer seasons, b) for winter seasons.

Figure A. 6: CO/NO$_X$ ratios stratified by year and season (summer: April to September, winter; October to March).

Figure A. 7: SO$_2$/NO$_X$ ratios stratified by year and season (summer: April to September, winter; October to March).

Figure A. 8: NO/NO$_2$ ratios stratified by year and season (summer: April to September, winter; October to March).

Figure A. 9: PM$_{2.5}$ (MAS) /PM$_{10}$ (HI) ratios stratified by year and season (summer: April to September, winter; October to March).

Figure A. 10: PM$_{2.5}$ (MAS) / NC$_{2.5}$ ratios stratified by year and season (summer: April to September, winter; October to March).
Figure A. 1: Spearman correlation coefficients for the relationship between SO₂ and other pollutants by year.
Figure A. 2: Spearman correlation coefficients for the relationship between NO and other pollutants by year and season, a) for summer seasons, b) for winter seasons.
Figure A. 3: Spearman correlation coefficients for the relationship between CO and other pollutants by year and season, a) for summer seasons, b) for winter seasons.
Figure A. 4: Spearman correlation coefficients for the relationship between O3 and other pollutants by year and season, a) for summer seasons, b) for winter seasons.
Figure A. 5: Spearman correlation coefficients for the relationship between PM$_{10}$ and other particulate pollutants by year and season, a) for summer seasons, b) for winter seasons.
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