

Seasonal Variability In Atmospheric Aerosol levels And Elemental Composition During 2006 At Uccle, Belgium

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Abstract. During 2006, a study was undertaken at Uccle, Belgium, to examine the boundary layer aerosol characteristics. As part of this study, PM_{2.5} and PM₁₀ aerosol samples were collected on 0.4 µm pore size Nuclepore polycarbonate filters. The collections were done during the daytime only and on days with no or few clouds. A total of 109 collections were performed with each sampler. The Nuclepore filters were analysed for the particulate mass (PM) by weighing, for black carbon (BC) with a light reflectance technique, and for up to 29 elements (from Na to Pb) by PIXE. Seasonal median atmospheric concentrations (and ranges) and seasonally averaged crustal enrichment factors (EFs, with Si as crustal reference element) were calculated. From examining these data, it appeared that (for both the PM_{2.5} and PM₁₀ aerosol) the median atmospheric levels of the PM and BC were about a factor of two higher in winter than in the other three seasons. The medians for the crustal elements (Al, Si, Ca, Ti) were similar in all seasons; for the primary biogenic element P and the essentially anthropogenic element V the highest medians were noted in summer; and still other (mostly anthropogenic) elements, including K, Mn, Fe, Cu, Zn, and Pb, had highest medians in winter, followed by fall; the medians for Zn and Pb in fall were about a factor of 2 higher than those in summer. The crustal EFs showed the same seasonal patterns as the concentrations. Several variables were highly ($r > 0.75$) correlated with each other. This was for example the case between PM_{2.5} Pb and the PM_{2.5} levels of BC, K, Mn, Fe, Cu, and Zn.

Keywords: atmospheric aerosols, PM₁₀/PM_{2.5}, chemical composition, seasonality, Belgium.

INTRODUCTION

In 2006, a study was undertaken at Uccle to examine the relationship between the vertical column-integrated Aerosol Optical Depth (AOD), the boundary layer aerosol characteristics, and the meteorological parameters, including air mass origin and mixing height. Continuous measurements of the AOD were performed at 5 wavelengths (from 306 to 320 nm) with a Brewer ozone spectrophotometer [1]. Next to this instrument, four filter samplers (two with PM_{2.5} inlet and two with PM₁₀ inlet) with either Nuclepore polycarbonate filters or quartz fibre filters were set up to obtain aerosol samples for gravimetric determination of the particulate mass (PM) and for detailed chemical aerosol characterisation. The samples were collected during the daytime only and on days with no or few clouds when 50% or more valid AOD data were expected. A total of 109 collections were performed with each sampler. Here, we present

and discuss the results from the elemental analyses by PIXE of the Nuclepore filters and some other data for these filters. Emphasis is given to the examination of the seasonal variability in the atmospheric concentrations of the elements and the PM and of the seasonal variation in the crustal enrichment factors. Pairwise correlations between the elements were also calculated and are briefly discussed.

EXPERIMENTAL

The AOD measurements and aerosol collections were done on the roof of the Royal Meteorological Institute (RMI) at Uccle near Brussels. This site can be classified as an urban background site [2]. The RMI is at 50°48'N, 4°21'E, and 100 m above sea level, and the roof is at 17 m above ground level. The four samplers deployed were all operated with 47-mm diameter filters and at a flow rate of 17 L per min. In two of four samplers (one with PM_{2.5} inlet, the other with

PM10 inlet) a 0.4- μm pore size Nuclepore polycarbonate filter was used as collection substrate. Of the 109 parallel aerosol collections, 20 were made during winter (January and February), 32 in spring (March, April, and May), 20 in summer (July and August) and 37 in fall (September, October, and November). The collection time per sampling varied from 4.5 to 12 hours, with median of 7.5 hours, and was longest in summer and shortest in winter. The average ambient temperature (and associated standard deviation) during the samplings was 2.7 ± 2.5 °C, 8.3 ± 4.7 °C, 24.3 ± 4.3 °C, and 16.2 ± 5.1 °C during winter, spring, summer, and fall, respectively. The fall temperatures were abnormally high for Belgium, and also in other West-European countries fall was abnormally warm. Furthermore, winter was somewhat abnormal in the sense that there was a strong air pollution episode with high PM levels at the end of January and beginning of February, which persisted from western to central Europe.

The Nuclepore filters were analysed for the PM by weighing, for black carbon (BC) with a light reflectance technique, and for up to 29 elements (from Na to Pb) by PIXE. The weighings were done at 20°C and 50% relative humidity and the filters were pre-equilibrated at these conditions for at least 24 hours. Details upon the light reflectance technique used for BC and upon the PIXE analyses can be found in [3] and in the references therein. Although also PIXE data will be reported here for Na and Mg, it should be indicated that these data have a large associated uncertainty because of strong matrix effects (i.e., X-ray attenuation and particle size effects).

RESULTS AND DISCUSSION

Concentrations And PM2.5 To PM10 Ratios

The median concentrations (and interquartile ranges) of the PM10 mass concentration for the PM, BC, and 18 elements in the four separate seasons are shown in Figure 1. For the PM, BC, and several elements, including S, K, Mn, Fe, Zn, and Pb (and to a lesser extent also Ni and Cu), clearly higher atmospheric levels were observed in winter than in the other three seasons. A similar picture was observed for the PM2.5 size fraction (not shown). Several of the above elements (i.e., K, Mn, Fe, Cu, Zn, and Pb) had their second highest median in fall; the medians for Zn and Pb in fall were about a factor of 2 higher than those in summer. For the typical crustal elements (Al, Si, Ca, and Ti) there was little difference between the different seasons and for the primary biogenic element P and the essentially anthropogenic element V the highest medians were noted in summer. The differences in the seasonal patterns of the PM and the various elements indicate that the atmospheric levels were not only controlled by the occurrence of surface temperature inversions. Seasonal variations in source strengths and/or air mass origin clearly also contributed to the observed differences.

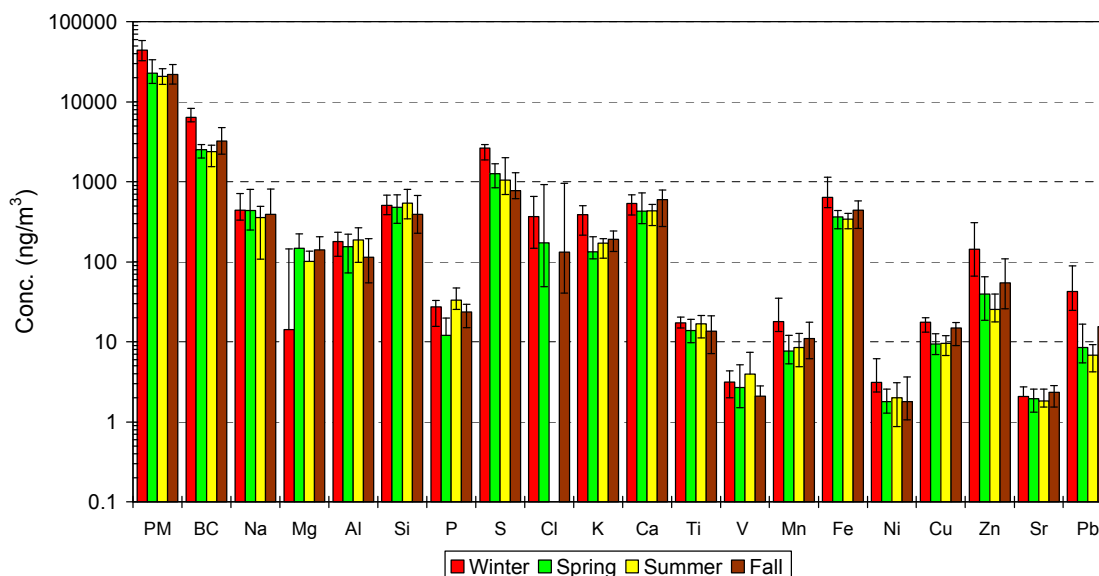


FIGURE 1. Medians (and interquartile ranges, denoted by the error bars) of the PM10 mass concentration for the PM, BC, and 18 elements in the four separate seasons for the 2006 samplings at Uccle, Belgium.

The PM, BC, and several elements were predominantly present in the PM_{2.5} size fraction of the PM₁₀ aerosol. For the PM, the average PM_{2.5}/PM₁₀ ratios (and associated standard deviations) were 0.81 ± 0.08 , 0.60 ± 0.14 , 0.55 ± 0.14 , and 0.54 ± 0.12 , in winter, spring, summer, and fall, respectively. For BC, the average PM_{2.5}/PM₁₀ ratio (average over all samples) was 0.94 ± 0.12 and there was virtually no change in this ratio with season. Also for some typical anthropogenic elements (such as S and Pb) there was no change in the ratio with season. Of the 18 elements depicted in Figure 1, only 6 (i.e., S, K, V, Ni, Zn, and Pb) had, on average (over all samples), most of their PM₁₀ mass in the PM_{2.5} size fraction. This suggests that these elements have a substantial contribution in the fine fraction from anthropogenic high-temperature sources (including gas-to-particle conversion for S). For the typical crustal elements Al, Si, Ti, the overall average PM_{2.5}/PM₁₀ ratio was around 0.2 and for Ca it was 0.16, which is all consistent with mineral dust dispersal (including both soil and road dust) as the dominant source process for these elements.

Crustal Enrichment Factors

Crustal enrichment factors (EF-values), relative to the average crustal rock composition of Mason and Moore [4] and with Si as reference element, were calculated for each individual PM_{2.5} and PM₁₀ sample. The seasonally averaged EFs for the PM_{2.5} size fraction are shown in Figure 2. Overall, the EFs follow the same seasonal pattern as the atmospheric

concentrations; this is not surprising considering that there was virtually no seasonal variation in the Si levels. The EFs of Figure 2 can be compared with those obtained in 1993-1995 for the PM_{2.0} size fraction at other sites in Belgium (i.e., an urban background site in Ghent and a near-city background site in Waasmunster) [3]. Overall, the EFs for Uccle are quite similar to those in that earlier study, thus indicating that the sources and source processes for the elements shown in Figure 2 are similar for the 3 sites and have not changed much over the course of more than 10 years. The largest differences (about a factor of 2) are noted for BC and Pb, with the data for Uccle being lower. The decrease for Pb is likely related to the complete phasing out of leaded gasoline in Belgium.

Although the average EFs for Ca in Figure 2 (and also in PM₁₀) are substantially larger than 1.0 (they range from 6 to 9 in PM_{2.5} and from 7 to 10 in PM₁₀), most of the Ca is likely from crustal origin, as is suggested by the low PM_{2.5}/PM₁₀ ratio for this element and by the good correlation of Ca with Si, Al, and Ti in the PM₁₀ aerosol (see below). The high EF indicates that the local/regional soil in Belgium has a composition which differs from that of average crustal rock and is enriched with limestone (CaCO₃) dust. Also Fe has average EFs, which are clearly higher than 1.0 (ranging from 7 to 16 in PM_{2.5} and from 4 to 8 in PM₁₀). Here, there is definitely a noncrustal contribution, as indicated by various inter-element correlations (see below).

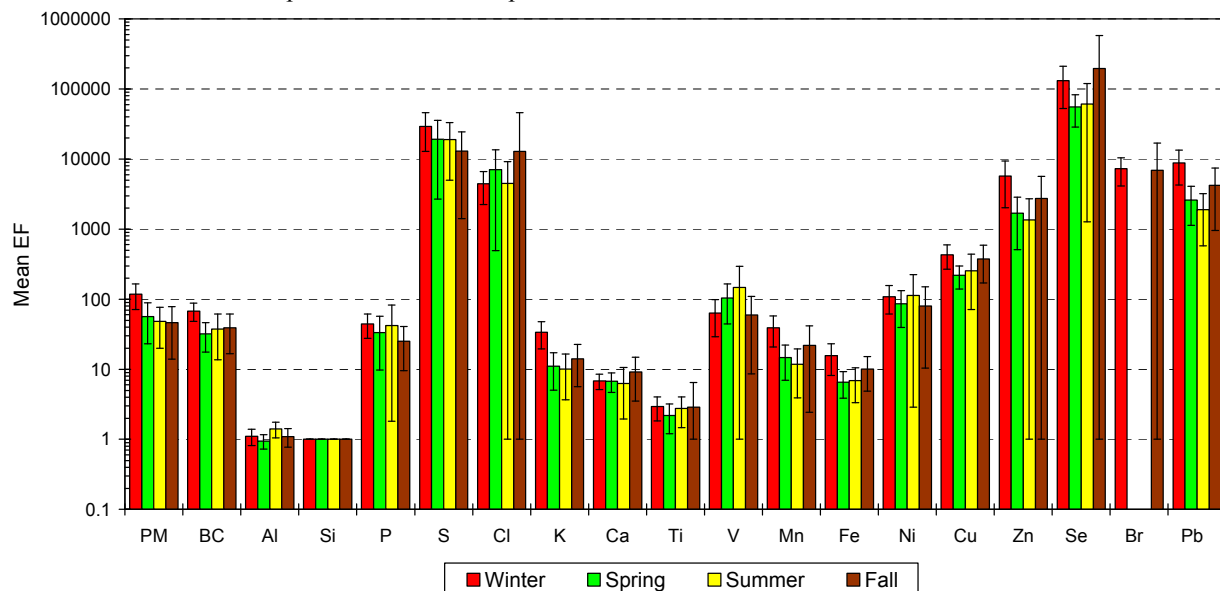


FIGURE 2. Average crustal enrichment factors (and standard deviations, denoted by the error bars) for the PM_{2.5} size fraction in the four separate seasons for the 2006 samplings at Uccle, Belgium. The data for BC are BC/Si concentration ratios.

Correlations

Pairwise correlations between the PM, BC, and the various elements were calculated in each of the two size fractions. In addition, various scatter plots between pairs of elements were constructed. In both PM_{2.5} and PM₁₀, PM was highly ($r > 0.75$) correlated with BC, S, and K; in both sizes, BC was highly correlated with PM, K, Mn, Fe, Cu, and Pb; and Pb was highly correlated BC, K, Mn, Fe, and Zn (and in PM_{2.5} also with Cu). This all, together with the large crustal EFs, suggests that a substantial fraction of these elements and of the PM is from anthropogenic sources, whereby there are likely several different individual sources or even source types; the high correlations may result from the fact that the major sources are located in the same direction or sector with respect to the sampling site, so that the coherent variation in concentrations is due to changes in wind direction or air mass advection. For example, although the correlation coefficient between Zn and Pb in PM_{2.5} was excellent (with r : 0.90) and also a scatter plot between both elements indicated that the correlation was real and not due to one or a few high data pairs, there was quite some variability in the Zn/Pb ratio (its 5-95% percentile range was 1.4-7.4 in PM_{2.5} and 1.5-8.0 in PM₁₀), suggesting that there is more than one dominant source (or source type) for these elements.

Si was highly ($r > 0.75$) correlated with Al and Ti in PM_{2.5} (and in PM₁₀ also with Ca), which is consistent with a predominantly crustal origin for these elements. Furthermore, an excellent correlation (with r : 0.87) was obtained between Na and Cl in PM₁₀, as would be expected if the two elements are mainly attributable to sea salt. That this is indeed the case can be concluded from the average Cl/Na ratio of 0.94 in PM₁₀, which is not too far from the Cl/Na ratio of 1.81 in bulk sea water [5], especially if one takes into account that Cl may be lost from the sea-salt aerosol in the polluted atmosphere [e.g., 6] and that there is a substantial uncertainty in the PIXE Na data.

Somewhat unexpectedly, V was poorly correlated with all other elements in both PM_{2.5} and PM₁₀. Heavy oil burning is an important anthropogenic source of both V and Ni [e.g., 7], so that both elements are often well correlated with each other. Here the correlation coefficients between both were only 0.47 in PM_{2.5} and only 0.40 in PM₁₀. The scatter plots between both elements indicated that the poor correlations were due to high Ni levels in a limited number of samples (in both PM_{2.5} and PM₁₀). For most of the samples, V and Ni were quite well correlated with a V/Ni mass ratio of about 2.5, which is consistent with a heavy oil burning origin. The excess Ni may be due to metallurgical (including non-ferrous) activities, as Ni showed correlation

coefficients ranging from 0.62 to 0.77 with the elements Mn, Fe, Zn, and Pb.

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