

**Geochemistry of PM10 over Europe during the EMEP intensive measurement periods in summer 2012 and winter 2013 – ACP2106-42**

**Reply to referee 3.**

*The authors thank the reviewer for the detailed review of the manuscript. The changes suggested have been addressed. We think that the manuscript has greatly improved after these changes.*

**This manuscript presents and discusses the composition of PM10 during intensive measurement periods in summer 2012 and winter 2013 for 20 rural background sites across Europe. The emphasis is placed on the mineral dust component, but data for several metals and metalloids are also given. Most of the data were obtained by particle-induced X-ray emission (PIXE). The study clearly shows that PIXE can provide a very valuable contribution in atmospheric aerosol research. The impact on mineral dust, which was often attributed to Saharan dust, on the PM10 aerosol and the spatial variation and seasonality therein are well discussed.**

**As discussed in detail below, the manuscript is on a few occasions unclear and it has some other weaknesses. There are also some problems with the references. Revision C1 is needed before this manuscript can be published in ACP.**

**Specific comments:**

**1. There are several gratuitous statements within the text with regard to the mineral dust and the non-crustal and non-sea-salt elements, which are not backed up by appropriate references. This is for example the case for the statement in line 66 on the composition of natural mineral dust and in lines 73-74 on the anthropogenic sources of mineral dust, for the attribution of the nssK to aluminosilicates (or to clays, as indicated in line 331) and to biomass combustion in lines 317-318, for the attribution of SO<sub>2</sub> to combustion processes in line 456 and for the attribution of part of the nss-sulphate to marine biogenic and volcanic emissions in line 457. Also, which combustion processes do the authors have in mind as source of SO<sub>2</sub>? Other examples of occasions with lacking references are given below.**

*Reply*

*We agree with the referee. References have been added in order to support the statements:*

*L66*

*Natural mineral dust mainly consists of silicate, carbonate, phosphate and oxide/hydroxide minerals derived from the erosion and weathering of rocks and soils (Moreno et al., 2008, Scheuvens et al., 2013). Mineralogical characterization of desert dust aerosols in Northern Africa carried out during the SAMUM campaign showed that the major constituents of the*

aerosol were quartz, potassium feldspar, plagioclase, calcite, hematite and the clay minerals illite, kaolinite and chlorite (Kandler et al., 2009, Scheuvens, et al., 2011).

L73-74

Mineral dust particles are also emitted by anthropogenic sources, such as agricultural activities, construction sites, mining, certain industrial activities such as the cement and ceramic industries, and road dust resuspension (Zender, et al., 2004).

L317

Non-sea-salt potassium (nssK) has a major aluminium-silicate affinity and may be present in minerals such as K-feldspars, muscovite and illite and clays (Scheuvens et al., 2013), but can also be emitted during biomass combustion (Andreae, 1983, McMeeking et al, 2009) .

L331

For those sites with a high correlation ( $R^2 > 0.9$ ) between nssK and Al, we consider that nssK is mostly associated with aluminium silicates. Given the low nssK-Al, the presence of illite or muscovite is likely (Scheuvens et al., 2011).

L456 & L457

Non-sea-salt sulfate is a major secondary component formed by the oxidation of SO<sub>2</sub>, mainly emitted by anthropogenic sources such as fossil-fuel combustion processes and metal smelters, as well as natural sources. Moreover, non-sea-salt sulfate (nssSO<sub>4</sub><sup>2-</sup>) may have a minor mineral association, mainly as coarse gypsum, and can also be released from marine biogenic and volcanic emissions (Bates et al., 1992 and references therein).

**2. Lines 48 and 587: Se is mentioned here (respectively in the Introduction and in the Conclusions) and concentration data for this element are given in Tables S3 and S4. However, this element is not discussed at all in the main part of the text. I suggest that it be discussed.**

Reply

The data have been revised and reinterpreted (see comment 12 below). These sentences have been changed by : "...high temperature processes (As, Pb, and SO<sub>4</sub><sup>2-</sup>) in Eastern countries,..."

Thanks to referee 3, Tables 3 and 4 were checked. We realized that average concentrations of some elements (Cu, Zn, As, Se, Br, Rb, Sr, Zr, Mo, Ba, Pb) for sites IE31, FR22, FR09, ES22 were shifted in the Table S3. We corrected the Table.

**3. Line 61: "Engelstaedter et al., 2006" is not in the Reference list. On the other hand, there is "Engelstaedter et al., 2009" in that list to which no reference is made within the text.**

Reply

- Reference for "Engelstaedter et al., 2006 has been included in the reference list and "Engelstaedter et al., 2009" has been removed

**4. Lines 107 and 153: "Lucarelli et al., 2010" is not in the Reference list. On the other hand, there is " Lucarelli et al., 2011" in that list to which no reference is made within the text.**

Reply

- The correct reference is Lucarelli et al., 2011; is has been replaced in the text

**5. Lines 168-169: It is somewhat unclear for which elements the concentrations were close to the analytical detection limit; besides, in which technique were those elements close to the detection limit, in PIXE or in IC-AES/MS or in both techniques?**

Reply

The sentence was certainly unclear; it has been modified as follows:

Correlations were lower for V, Cr, Pb and Sr ( $R^2 = 0.60-0.69$ ; slopes 0.3 to 0.9), and very low for Ni ( $R^2 = 0.19$ , slope 0.4; see Fig. S1 and Table S2 in the Supplementary Information). For all those elements, concentrations were close to the MDL in PIXE:

Caption of Table S1 was also modified: "Table S1: Average minimum detection limit (MDL) for the elements measured by PIXE."

**6. Line 188: A literature reference is needed for the Na/Cl ratio of 0.56 in sea water.**

Reply

Reference "Drever 1997" has been added

**7. Lines 280 and 285: A literature reference is needed for the attribution of (part of the) Al, Si and Fe to a clay-dominated source and to illite.**

Reply

The reference Scheuvens et al., (2011) has been added

**8. Lines 292-296: Literature references are needed for these statements on Ca.**

Reply

The text has been modified as follows:

$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ , and/or anhydrite ( $\text{CaSO}_4$ ) or as silico-aluminates (Ca-plagioclase) (Scheuvens et al., 2013). This element is usually related to natural sources (soil resuspension), although it can be emitted by a number of anthropogenic sources, such as road dust and construction activities (Amato et al., 2009). Calcium carbonate may interact with acidic compounds in the atmosphere forming coarse secondary calcium nitrates ( $\text{Ca}(\text{NO}_3)_2$ ) and calcium sulphates ( $\text{CaSO}_4 \cdot x\text{H}_2\text{O}$ ) (Dentener et al., 1996, Krueger et al., 2004, Alastuey et al., 2005, Hwang and Ro, 2006).

**9. Lines 308-309: A literature reference is needed for this statement on nssMg.**

Reply

The text has been modified as follows:

The nssMg may be associated with clays, carbonates (dolomite), aluminium-silicates or salts (Scheuven et al., 2011).

**10. Line 381: There is something missing in between "during" and "account".**

Reply

“...dust during the sampling period account...”

**11. Line 452: What is the basis for attributing part of the K<sub>2</sub>O to biomass burning? It is known that KCl is a form of K that is present in pyrogenic particles.**

Reply

K<sub>2</sub>O has been replaced by K

**12. Line 519: As has besides coal combustion other sources that are of similar or even higher importance, such as Pb production and especially Cu-Ni production (Nriagu and Pacyna, 1988).**

Reply

Yes; this comment is very pertinent. Actually we have revised the data interpretation and identified higher correlations of As with other elements such as Pb. Initially we did not consider the French sites for this analysis and the correlation As/Se was more significant. However, when these sites were considered this correlation decreased. The following sentence has been included in the text:

“A similar trend was also observed for pollutants such as Pb (see Tables S3 and S4). Sources of As, Pb, and SO<sub>2</sub> (and other volatile pollutants such as Cd, Se, and Hg) are related to high-temperature processes such as coal combustion, roasting and smelting of ores in non-ferrous metal smelters (Pb and Cu-Ni production) and melting operations in ferrous foundries, among others (Pacyna, 1986, and Nriagu and Pacyna, 1988).”

Corresponding sentences in the abstract and in the conclusion sections were modified (as indicated in comment 2).

**13. Line 573: It is unclear what MSY and MSC denote.**

Reply

MSY and MSC refer to the Montseny and Montsec sites. They have been replaced by ES1778 and ES22, which are the EMEP codes used in the manuscript.

**14. Figure 12: It is unclear what SW, SC and CE denote.**

Reply

*Caption has been modified, replacing "SW and SC" by "Southwestern and Central Southern Europe" and CE by "Central Europe"*

*Figure 12: Ternary diagram for major mineral dust components (SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>) and SO<sub>4</sub><sup>2-</sup> for days with (left, SDE) and without impact of SDE (right, non-SDE). Orange: GR02; red: sites; purple: Central Western Europe; black: Central Europe sites; blue; Northern Europe and Atlantic sites; green: Eastern Europe sites; empty symbols: high altitude sites.*

*This change has also been made for Figures S5, S6, and S10*

## **15. Technical and other minor corrections:**

*Reply*

*All the technical corrections have been applied*

- line 59: the "-1" of "year-1" should be in superscript. - *DONE*
- line 92: the "-2" of "m-2" should be in superscript. - *DONE*
- line 97: subscripts and superscripts are needed for "SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, NH<sub>4</sub><sup>+</sup>". - *DONE*
- line 141: replace "additionally to" by "addition for". - *DONE*
- line 157: replace "andboth" by "and both". - *DONE*
- line 168: replace "S<sub>2</sub>in" by "S<sub>2</sub> in". - *DONE*
- line 259: replace "10%PM<sub>10</sub>" by "10% of PM<sub>10</sub>". - *DONE*
- line 334: replace "SDE in" by "SDEs in". - *DONE*
- line 382: replace "µgPM<sub>10</sub>" by "µg PM<sub>10</sub>". - *DONE*
- line 430: replace "see Fig.s" by "see Figs.". - *DONE*
- line 440: replace "but whereas" by "whereas". - *DONE*
- line 471: replace "contribution of" by "contributions of". - *DONE*
- line 476: replace "indicate a low" by "indicating a low". - *DONE*
- line 483: replace "Concentrations" by "The concentrations". - *DONE*
- line 496: replace "with Nickel" by "with nickel". - *DONE*
- line 515: replace "see Fig.s" by "see Figs.". - *DONE*
- line 519: replace ".As shown" by ". As shown". - *DONE*
- line 530: replace "see Fig.s" by "see Figs.". - *DONE*

- titles of journal articles in the Reference list should be in lower case instead of in Title Case (e.g., for Aluko and Noll, 2006). - *DONE*

- for authors with two initials in the Reference list, there should be a space between the two initials (e.g., in lines 624, 637, 680). - *DONE*

- line 614: replace "L. C. L. C." by "L. C.". - *DONE*

- line 640: replace "Health 2012;" by "Health,". - *DONE*

- line 648: replace "J Geophys Res 114" by "J. Geophys. Res., 114". *This references was removed*

- line 681 replace "U S A 108:" by "U S A, 108, ". - *DONE*

- line 684: replace "andGanor" by "and Ganor". - *DONE*

- line 691: replace "B 318, (2014)" by ", B 318,". - *DONE*

- line 692: replace "B 363" by ", B 363". - *DONE*

- line 695: replace "Environ Health Perspect 2011;" by "Environ. Health Perspect.,". - *DONE*

- line 732: replace "Rev Geophys 40:1002" by "Rev. Geophys., 40, 1002--". - *DONE*

- Table 1: it is unclear what the "P" in the Filter column denotes; presumably "Partisol"; in any case, it should be indicated what it denotes. - "P" refers to Pallflex. Indicated in the caption.

- Caption of Figure 8: replace "proportional to the concentrations" by "proportional to the concentrations and percentages". - *DONE*. Change also done in caption of Figures 3, 6 and S4.

Reference J. O. Nriagu and J. M. Pacyna, Quantitative assessment of worldwide contamination of air, water and soils by trace metals, *Nature*, 333, 134-139, 1988. - *Reference added*

**For the Supplementary Information:**

- Heading of Tables S3 and S4: the "-3" of "m-3" should be in superscript. - *DONE*

- Caption of Figure S1: it is unclear what MSY denotes. - *DONE*

- Caption of Figure S4: replace "proportional to the concentrations" by "proportional to the concentrations and percentages". - *DONE*