

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

Reply to Prof. Joseph Prospero.

Authors thank Professor Joseph Prospero for his valuable comments. We have taken into consideration his suggestions which have enabled us to considerably improve the manuscript. In the paragraphs below we detail the changes addressed.

General Comments:

The authors present the results obtained in the third intensive measurement period (IMP) which took place in the summer of 2012 and winter 2013. PM10 filter samples were concurrently collected at 20 regional background sites across Europe and were subsequently analyzed for their mineral dust content. Because of the uniformity in protocols, they were able to view the data in a coherent way which allowed them to associate composition and concentration patterns to specific generic source types. Mineral dust was a special focus of the study. Dust concentrations were greatest in the southern and easternmost countries, accounting for 20-40% of PM10. This regional impact is largely attributed to Saharan dust outbreaks which were responsible for the high summer dust loadings at western and central European sites. The spatial distribution of some components and metals reveals the influence of specific anthropogenic sources on a regional scale. Particularly notable was the identification of the impact of shipping emissions (V, Ni, and SO₄) in the regions bordering the Mediterranean. They were also able to identify the impacts of metallurgy sources (on Cr, Ni, and Mn), and coal combustion (As, Se, and SO₄), and traffic (Cu).

The paper highlights the role that mineral dust might play in air quality issues and, thus, human health. On the basis of this paper, it is clear that in some European regions African dust could be an important issue in air quality. However it also shows that mineral dust is a significant contributor in other regions that are not likely to be heavily affected by African dust but rather that local and regional dust sources are significant. Because of the strong focus of this paper on dust and the coherent data set obtained over a large area, it is a unique contribution to the field of air quality.

The paper presents a great deal of information that can make it difficult to see linkages and associations. In general the authors do a good job in identifying such relationships although in some sections this could possibly be done more clearly. They provide many excellent graphical products which facilitate interpretation.

One aspect that is missing from the paper is the sense of the larger context - how the European results compare with similar studies in other regions. There is some review of this aspect in the introductory sections but there is no follow up on this with their own results.

To provide a larger context, perhaps the authors give discuss how the dust activity in the IMP periods compares with dust activity in general during the year and how this year (i.e., experimental "year") compares with other years. This links their work to the general question of variability (and of course to the issue of climate change). I am not suggesting that these issues have to be addressed in any depth, but they might be touched on to provide a sense of scale. In general the paper is well organized and clearly and succinctly written. It makes a significant contribution to the field of aerosol properties and air quality. The data set are unique in their coverage and coherence.

There are no major problems with this paper and it warrants publication.

Specific Comments:

1. In the section beginning at about 238 and in Fig. 8 and Fig. 9, they discuss the mean levels of dust concentrations measured at various sites. I was surprised that concentrations were not higher and the time-spread of the events was relatively short. They point out for example (ca. line 381) that at the Spanish sites the contribution of Saharan mineral dust accounts for two exceedances of the WHO 24-hour guideline of 50 $\mu\text{gPM}_{10} \text{ m}^{-3}$. It is interesting to compare these data with the measurements of PM₁₀ in the Caribbean [Prospero et al., Global Biogeochemical Cycles, 2014] where the PM₁₀ exceedances are frequent and driven by African dust. At Caribbean sites the guideline is exceeded on about 10% of the days on an annual basis and as much as 20 - 35% of the days during the peak dust months.

Reply

Yes, surprisingly, the number of exceedances can be considered as low if compared with other more distant areas also impacted by Saharan dust outbreaks such as Barbados, where frequent exceedances of the PM₁₀ daily limit value occur related to the Saharan dust outbreaks (Prospero et al 2014). This is commented in the conclusion section in the new version of the manuscript (see below).

In Section 3.2.2 Mineral dust: 270: "In Eastern Europe, where Saharan dust events did not impact PM levels, a local/regional dust source is deduced." I would have expected some impact. Models and satellite products do show dust events penetrating the region but perhaps the African dust gets lost in the regional soil "noise".

Reply

Yes we have modified this sentence. The impact of the Saharan dust event in Eastern Europe cannot be discarded but, the high contribution of regional/local dust, as deduced from the elevated concentrations and from the geochemical signatures, obscures the evidence of the SDEs.

2. 350: 3.3 Mineral dust contribution: impact of Saharan dust events Here the authors summarize and discuss the dust loads measured across the network of stations. As I noted above, the concentrations of dust in the Caribbean are higher than this. I wonder how much of the dust at the European sites is greater than PM₁₀. I note for example that the two big

dust events (June-July 2012 and Jan 2012 as shown in Fig. S3) are low-level transport events. I would suspect that there is a considerable component above 10µm diameter. Are there any measurements of the complete size distribution either during the experiment periods or obtained at other times? Although this might not be relevant to the discussion of PM10 it might provide some insights on the general nature of the impact of African dust on health.

Reply

Unfortunately, there were no measurements of the coarser fraction (>10 µm) during the sampling periods. Actually, in recent years, more studies on the impact of Saharan dust on air quality in Europe have focused on PM10, although, as far as the authors are aware, there are not many studies simultaneously measuring PM10 and TSP during Saharan dust events. A study carried out in the Iberian Peninsula (Rodríguez et al., 2001) concluded that TSP concentrations could be considered as representative of the regional PM10 levels in the rural environment during Saharan dust events, indicating a relatively low contribution of the coarser fraction (>10µm). However, simultaneous measurements of PM10 and TSP were not performed at any site in this study by Rodríguez et al. Moreover, the size ratio may vary depending on the source and transport scenario (e.g. depending on the altitude of transport) so that a significant contribution of coarse PM cannot be discarded.

As regards the health effects of Saharan dust, most studies carried out in Europe have focused on PM10, PM2.5 and/or PM2-5-10, as summarized in the review by Karanasiou et al., 2012. These authors concluded that the health impact of Saharan dust outbreaks needs to be further explored. Therefore, the impact of Saharan dust events on TSP and health outcomes of the coarser fraction (PM >10µm) should be further investigated.

References (already in the list)

Rodríguez, S., Querol, X., Alastuey, a., Kallos, G. and Kakaliagou, O.: Saharan dust contributions to PM10 and TSP levels in Southern and Eastern Spain, Atmos. Environ., 35(14), 2433–2447, doi:10.1016/S1352-2310(00)00496-9, 2001.

Karanasiou, A., Moreno, N., Moreno, T., Viana, M., de Leeuw, F. and Querol, X.: Health effects from Sahara dust episodes in Europe: literature review and research gaps., Environ. Int., 47, 107–14, doi:10.1016/j.envint.2012.06.012, 2012.

3. The authors do a commendable job in providing a good array of figures (in the paper and in the supplement) that summarize and synthesize the results of their analyses. The ternary diagrams are particularly effective in this regard. They show for example that with respect to SiO₂, Al₂O₃ and Fe₂O₃ (Fig. S5), in dust events the average composition was almost identical for all sites, indicating a similar silico-aluminous composition. The large variability in the contribution of CaO stands out. They relate this to changes in source areas. The uniformity in the composition of long-range-transported African dust has been previously noted, e.g., Trapp et al., Marine Geochem (2010). However I would expect that the European sites might see more variability in trace species in their dust because they are more likely to be impacted by dust from specific sources (as seen in some of the satellite images in Fig. SXXX).

In contrast, by the time dust crosses the Atlantic to the Caribbean, the dust from different sources will have been more mixed.

Reply

Yes, the homogeneity observed for dust composition during the summer episodes is surprising. The following sentence, comparing this result with previous results obtained at more distant areas, such as Barbados or Miami, is included in the text, in the conclusion section:

“These results are consistent with those obtained from dust collected on Barbados during Saharan dust events, showing a high uniformity of dust composition that was attributed to the mixing during transport of dust originating from different source areas (Prospero and Lamb 2003, Trapp et al., 2010, Muhs et al., 2014).”

As regards variations in CaO contribution: the higher contributions of CaO observed during the winter IMP, as compared with the summer IMP, were attributed to differences in source area. However, during the summer IMP differences in CaO relative contributions at the different sites were attributed to two different causes: 1) higher contribution of local Ca in certain locations (IT01 and ESCL1); 2) preferential deposition of coarse calcium carbonate particles, resulting in higher contributions of CaO in the southern sites. This has been clarified in the revised text.

References added:

Prospero, J. M. and Lamb, P. J.: African droughts and dust transport to the Caribbean: climate change implications. Science 302:1024–1027, 2003.

Trapp, J. M., Millero, F. J. and Prospero, J. M.: Temporal variability of the elemental composition of African dust measured in trade wind aerosols at Barbados and Miami, Mar. Chem., 120(1-4), 71–82, doi:10.1016/j.marchem.2008.10.004, 2010.

Muhs, D. R., Prospero, J. M., Baddock, M. C., Gill, T. E., Muhs, D. R., Prospero, J. M., Baddock, M. C. and Gill, T. E.: Identifying Sources of Aeolian Mineral Dust: Present and Past, , in: Knippertz, P. and Stuut, J. W. (Eds): Mineral Dust: A Key Player in the Earth System, Springer Science Business Media Dordrecht 2014.

4. 456 et seq.: This section and the discussion about dust-Ca-SO₄ is not clear. I would not expect to see much primary gypsum. But I would expect to see varying amounts of gypsum produced from reactions with SO₂/SO₄. I see what they are trying to do in this section but it does not come across clearly. What is the conclusion? That there is little or no primary gypsum? Figure S7 is very confusing. How did they decide to draw regressions between specific points as they did. Maybe the explanation is buried in the text. Some text should be provided in the caption.

Reply

Yes, the discussion was not clear enough; Figure S7 has been deleted. The contribution of primary gypsum is very minor, as deduced from low concentrations at mountainous sites. The relative concentrations of sulfate increase with distance indicating that it can be attributed to the contribution of secondary anthropogenic sulfate.

5. 495: Section 4. Conclusions This section is a straight-forward recapitulation of the major points of the paper. But as I stated in the general comments, I would have liked to have seen

more in the way of broadening the perspective of the results, to place the results in the larger picture of dust-health issues. I recognize that the paper is by its nature focused on a specific objective. But it would be nice to round it out with a broader context

Reply

We have tried to improve this section. We have included a sentence about the impact of African dust in Europe, its contribution to PM10 and the inter-annual variability of these contributions. The results are compared to those obtained in Barbados (Prospero et al 2014).

We have also included in this section the discussion regarding the homogeneity in composition of dust during the African episodes.

We have also highlighted the contribution of regional / local sources of mineral dust to PM10 in southern and eastern areas of Europe, accounting for 10-25% of PM10 during the NON-SDE periods.

Reference added:

Prospero, J. M., Collard, F.-X., Molinié, J. and Jeannot, A.: Characterizing the annual cycle of African dust transport to the Caribbean Basin and South America and its impact on the environment and air quality, Global Biogeochem. Cycles, 28(7), 757–773, doi:10.1002/2013GB004802, 2014.

Technical Corrections.

Figure S5. What is "CadO" in the top right ternary diagram? Some other aspects of the diagrams also should be explained such as the factors used, e.g., "CadO dust*1.2"; "K2O dust*3.5".

Reply

This was a mistake. CadO corresponded to CaO. It has been corrected.

As regards for the estimation of the factors used in the ternary diagrams: The average concentrations for each element or specie were calculated considering all sites. Then, the average concentration of each element/specie was multiplied by a factor in order to obtain a similar average concentration value for all the elements/species. To this end the average concentration of Al2O3 was taken as a reference. Thus the concentrations adjusted to place the average composition in the center of the triangle for each diagram.

Figure S8 is very complex. But the authors point out the very significant difference in V and Ni over the Mediterranean region as contrasted to other regions. This stands out nicely in the graphs, complex as they are.

Reply

Yes we know that it is complex but we think is the best way to show the differences.

Figure 10 caption: "Figure 10: Average composition (absolute values – $\mu\text{g m}^{-3}$, top and relative contribution –%, bottom) of mineral dust at selected sites when affected by African dust episodes. Results from both summer and winter (GR02-W) IMPs are included." Better: Figure 10: Average CONCENTRATION OF MINERAL DUST COMPONENTS (absolute values – $\mu\text{g m}^{-3}$, top-) and THE relative contribution of components (% , bottom) IN mineral dust at selected sites when affected by African dust episodes. Results from both summer and winter (GR02-W) IMPs are included.

DONE