

## **Review of “Aerosol trace element solubility and deposition fluxes over the polluted, dusty Mediterranean and Black Sea basins” by R. Shelley et al.**

Shelley et al. present a novel dataset of trace metals and P solubility and dry atmospheric fluxes from aerosols collected during GA04 cruise in Mediterranean (Med) and Black seas. It is interesting to have atmospheric data useful for studies on air-sea exchange in these regions which are influenced by various aerosol sources, notably with a gradient between East and West,.

The manuscript is well-written, logically organized, and adequately illustrated. Abstract is succinct and accurate. The discussion focuses in part on the comparison between the values found in the Med and Black Seas compared with the ones obtained in Atlantic Ocean, where the authors took part in several cruises. This comparison is interesting in order to situate the anthropogenic contribution in these two regions, which are not at the same distance from pollution sources. It would also have been useful to have a discussion in this context with the other measurements made in the Mediterranean, in particular for deposition fluxes. There is extremely little data available from campaigns at sea, but there are several observatories on islands with long-term measurements in these regions, e.g. Finokalia, Lampedusa or data from annual monitoring: Corsica, Balearic island.... A small putting in context and comparison with previous and recent works (since the data have been obtained in 2013) could be invaluable to get the most out of these data.

Overall, the quality of the figures is not very good, but I think this is due to the changeover to pdf format and should be sorted out in the final manuscript.

### **Specific comments:**

**Title:** Because of their location, the Mediterranean and the Black Sea are usually subject to polluted or desert dust-laden masses. In the case of this paper, no specific or intense events of desert dust or pollution have been reported. So I think the title could be simplified: “Aerosol trace element solubility and deposition fluxes over the Mediterranean and Black Sea basins”

**Figure 1:** In order to have a better view of the transect and the sampling zones, it would be useful to zoom in on the measurement area over sea (e.g., between 50°N and 25°N) and refine the thickness of the aerosol track.

It would be also useful to include the numbers of the filters that are noteworthy and discuss them in the text, for example, samples 18 and 20, which stand out in terms of soluble concentrations.

**SC-01. Line 95-134.** The description of the field blanks (sampling and analysis) is clear, but there is no clear explanation regarding the use of the blank values. Are they subtracted from the total and soluble values? If so, which 'type' of blanks (1, 2, or 3)?

**SC-02: Line 50:** “For our flux calculations, we used  $v_d$  values of  $1 \text{ cm s}^{-1}$  for the lithogenic elements and  $0.1 \text{ cm s}^{-1}$  for the anthropogenic elements”. The data show that certain elements are predominantly crustal during desert dust events (see EF values), whereas they are anthropogenic at other times. It would be interesting to calculate the percentage of desert dust inputs compared to anthropogenic inputs during the campaign. If it is significant, in order to better constrain the flux calculations, shouldn't these dust events (i.e.  $v_d$  values of lithogenic) be taken into account in the flux calculations for these elements?

**SC-03: 3.1. Air mass origins during GA04 :**

The analysis of back-trajectories is useful for classifying the different samples based on potential sources, but a more detailed analysis of the actual sources might help better understand the various influences in the discussion section. To aid data analysis in the case of desert dust arrivals, it would be interesting to examine dust emissions, using observations such as RGB SEVIRI, along the back-trajectories, rather than relying on PSAs which do not provide information on the actual origin of the transported dust. Indeed, just because an air mass passes over potentially emitting areas does not mean it picks up desert dust; the winds must be strong enough to trigger dust production. For example, in the case of sample 38, the air mass passes over both Tunisia and Algeria, which are two emissive sources with quite different mineralogical characteristics. The Tunisian source is richer in calcite, which can play a role in neutralizing acids (Kandler et al., 2007). It could be invaluable to consider this point in the discussion of acid effect on solubility.

*Kandler, K., Benker, N., Bundke, U., Cuevas, E., Ebert, M. and co-authors. 2007. Chemical composition and complex refractive index of Saharan Mineral Dust at Izaña, Tenerife (Spain) derived by electron microscopy. Atmos. Environ. 41, 8058–8074.*

**Figure 2:** This figure is complex enough. To clarify Figure 2, perhaps using only the back-trajectories at 10 meters might be sufficient since the collection takes place at the height of the ship? Furthermore, the text does not explain which altitude (10, 500, or 1000 meters) is used as the reference for classifying the air masses. It would be useful to specify, if possible, the altitudes of the boundary layer during the campaign, as the back-trajectories at 1000 meters are only relevant if the boundary layer reaches at least 1 km and is well mixed during the sampling?

Could you add the filter numbers at the beginning and end of the back-trajectory types to Figure 2 to link this figure with the subsequent ones, especially in the area where the routes of legs 1 and 3 overlap?

In the same idea, please color the bars in Figures 3, 4, 5, and 6 according to the air mass origins (rather than just the colored horizontal bar at the top of each panel). This would make it much easier for the reader to link the sample to its origin (which is the basis of your data analysis in the following sections). Since the names of the metals are labeled on each panel, it should not cause any confusion.

#### **SC-04 : Lithogenic elements**

**L180 :** Please indicate in the text the average value of metal concentrations (e.g., iron) in the NAF and non-NAF samples, so that these values can be used as a reference for metal concentrations according to their origin, and to quantify the contribution of Saharan air masses to the background metal levels during the campaign

**L200 and 201 :** I don't understand the connection between the first sentence and the given example since s-Fe concentrations in the RNA samples are lower than in the NAF samples.

**L200 to 205 :** In addition to the s-Fe values, include the average solubility value. This will help illustrate your discussion on the relationship between solubility and s-Fe concentrations.

#### **SC-05 : Anthropogenic elements**

**L219 :** add “, except P” before Fig.5

**L223 then 242:** “Soluble V and Ni concentrations were strongly correlated ( $r_2 = 0.973$ ,  $p = <<0.01$ ),

*which is consistent with V and Ni in aerosols being markers of shipping emissions, and these emissions being the dominant control on s-V and s-Ni concentrations (Becagli et al., 2012; Baker and Jickells, 2017)."*

Here, I think that it will be more precise to write: "Soluble V and Ni concentrations were strongly correlated ( $r^2 = 0.973$ ,  $p < 0.01$ ). V and Ni in aerosols being primarily attributed to shipping emissions (Becagli et al., 2012), this is consistent with the idea that these emissions are the dominant factor controlling s-V and s-Ni concentrations, as previously observed in the Atlantic Ocean (Baker and Jickells, 2017)."

In order to reinforce this conclusion, is there a correlation between the t-Ni and t-V values in the non-NAF samples that could confirm a source related to maritime traffic, as observed by Becagli et al. (2012)? It could be interesting to confirm (or not) the Becagli et al.'s conclusion obtained on local point in Med, on a large area of Med and Black seas. If it is not the case, the fact that s-Ni and s-V are correlated indicate that even if these metals can have different anthropogenic sources (that is highly possible in Med and consistent with your sentence L223-225), the 'shipping' source, is the primary contributor of soluble atmospheric inputs for these metals.

**L 225:** "suggesting that P (as well as V, Ni, Cu, Zn and Pb) has important non-dust sources": P could be issued from European dust source related to agricultural soils enriched in P by fertilizers. That could explain that t-P follows the behavior of lithogenic elements, even if the EF are  $>10$  (see e.g. Bergametti data in Mahowald et al. (2008)).

*Mahowald, N., et al. (2008), Global distribution of atmospheric phosphorus sources, concentrations and deposition rates, and anthropogenic impacts, Global Biogeochem. Cycles, 22, GB4026, doi:10.1029/2008GB003240*

**L233-235 :** It would be more correct to write : «... *that the Mediterranean and Black Sea atmospheres were still subject to significant anthropogenic influence of Pb emissions sources in 2013*», since these data are more than 10 years old (European anthropogenic Pb emissions decreased since the cruise, see e.g. annual European Union emission inventory report 1990-2022) and the emissions come from the proximity of various anthropogenic sources compared with the Atlantic.

**Figure 4 :** Authors explained that some values of solubility reach 300% due to probable contaminations. I am rather sceptical about the presentation of these values in the same way as the other values, since it's impossible to estimate the contamination and these values suggest that the solubility is high when it may only be a few %, for example. I think it would be clearer to show these values in "transparent" colour, rather than in the same colour as the uncontaminated values.

#### **SC-06 : Influence on element solubility**

**L298-309:** Your discussion is based on the acid effect from polluted species, but your dissolution protocol is also carried out in a buffered medium. To what extent could the excess acid affect the values you find?

Another point that raises questions in this part of the discussion, although the concentrations of inorganic acid and base species are higher than in the Atlantic, it is the capacity of these species to acidify or neutralise the aerosol, and therefore play on the pH, that will affect solubility. For this, it is not so much the concentrations that are important, but the balance of neutralisation of the inorganic (and organic) acidic species by the alkaline species (or vice versa). You use the  $nssSO_4/Fe$  ratio to estimate the excess of acid over Fe, but this is only valid if  $nssSO_4$  is not neutralised by  $NH_4^+$  or by the presence of calcite, for example, in your samples. In your case, as you do not have Ca values, you cannot estimate the neutralisation capacity linked to the presence of calcite in NAF samples, but you

can estimate the effect of  $\text{NH}_4^+$  in all your samples. It would be more accurate to use, for example, the neutralisation ratio (Silvern et al., 2017) rather than the  $\text{nssSO}_4/\text{Fe}$  value.

*Silvern, R. F., Jacob, D. J., Kim, P. S., Marais, E. A., Turner, J. R., Campuzano-Jost, P., and Jimenez, J. L.: Inconsistency of ammonium–sulfate aerosol ratios with thermodynamic models in the eastern US: a possible role of organic aerosol, Atmos. Chem. Phys., 17, 5107–5118, <https://doi.org/10.5194/acp-17-5107-2017>, 2017.*

**L314** : “Overall, the low solubility of Al, Mn, Fe, Co and Th in NAF samples (relative to similar samples collected over the Atlantic; Fig. 7) appears to be related to the short atmospheric transport pathway to the Mediterranean.” : The low solubility ‘could be’ related, this is one possible explanation but it would also be interesting to discuss the effect of other phenomena to explain this low solubility compared to the values in the Atlantic. First of all, the dust emitting sources are different between the samples taken in the Mediterranean (North of Africa) and those taken in the Atlantic (Morocco, Central Sahara, Bodélé, Sahel, etc.). The difference in sources (including the difference in mineralogy, particle size distribution and calcite load, and therefore pH) could also explain the differences you observe. You seem to consider that all Saharan emission sources have the same solubility (and should respond in the same way to the process along the transport route), but the data at the source show that the solubility of iron in particular can vary from one source to another (see e.g. Shi et al., 2011; Paris et al., 2010). In particular, the solubility in the first dust period appears to be lower than in the second NAF period, even though the route is comparable.

Moreover, unless I'm mistaken, most of the measurements made in the Atlantic were taken during a different period than the GA04 cruise and the seasonality of the sources is different. It would be interesting to specify this in the text, particularly as photochemical processes are probably accentuated in summer in the Med and the Black Sea. This could perhaps explain the differences in solubility in the case of non-NAF samples, e.g. linked to oxidation processes or to the greater presence of organic matter or potential mixing with anthropogenic forms.

*Shi, Z., et al. (2011), Influence of chemical weathering and aging of iron oxides on the potential iron solubility of Saharan dust during simulated atmospheric processing, Global Biogeochem. Cycles, 25, GB2010, doi:10.1029/2010GB003837*

*Paris, R., Desboeufs, K. V., Formenti, P., Nava, S., and Chou, C.: Chemical characterisation of iron in dust and biomass burning aerosols during AMMA-SOP0/DABEX: implication for iron solubility, Atmos. Chem. Phys., 10, 4273–4282, <https://doi.org/10.5194/acp-10-4273-2010>, 2010.*

### SC-07 Dry deposition

**L 331: “Dry deposition therefore probably accounts for the majority of total atmospheric fluxes to the basins over the study period.”** To reach this conclusion, rather than compare with the rainfall, it could be interesting to compare with the elemental fluxes obtained by wet or total deposition measurements in the same period in these areas. For example, if we consider an iron concentration of  $340 \text{ nmol.L}^{-1}$  in rain collected in June in the western Mediterranean (Desboeufs et al., 2022, it is just an example as base for the calculation ) with a rainfall of  $1 \text{ mm.d}^{-1}$ , this is equivalent to a flux of  $340 \text{ nmol.m}^{-2}.\text{d}^{-1}$ , i.e. in the average of values obtained here.

*Desboeufs, K., et al.: Wet deposition in the remote western and central Mediterranean as a source of trace metals to surface seawater, Atmos. Chem. Phys., 22, 2309–2332, <https://doi.org/10.5194/acp-22-2309-2022>, 2022.*

Only Guieu's work is cited, even though it dates from the early 2000s and several studies on deposition have since been carried out in these regions. Numerous measurements have been made in the Mediterranean and there is a great deal of data available (e.g. the long-term measurements in Finokalia, the literature on the total deposition in Sardinia, Corsica or Balearics Islands ). It is a pity that no comparison is provided with these data obtained on islands to see the potential differences with our data, notably about the source of trace metals and nutrients, which are studied in this literature, e.g.:

*Theodosi C., Markaki Z., Pantazoglou F., Tselepidis A., Mihalopoulos N., Chemical composition of downward fluxes in the Cretan Sea (Eastern Mediterranean) and possible link to atmospheric deposition: A 7 year survey, Deep-Sea Research Part II, 164, 89-99, 2019.*

*Desboeufs, K., Bon Nguyen, E., Chevaillier, S., Triquet, S., and Dulac, F.: Fluxes and sources of nutrient and trace metal atmospheric deposition in the northwestern Mediterranean, Atmos. Chem. Phys., 18, 14477–14492, doi.org/10.5194/acp-18-14477-2018, 2018.*

*Christodoulaki S., G. Petihakis, N. Mihalopoulos, K. Tsiaras, G. Triantafyllou, M. Kanakidou, Human-Driven Atmospheric Deposition of N and P Controls on the East Mediterranean Marine Ecosystem, JAS, 73, 1611- 1619, 2016.*

*Kanakidou M., S. Myriokefalitakis, N. Daskalakis, G. Fanourgakis, A. Nenes, A. Baker, K. Tsigaridis, N. Mihalopoulos, Past, Present and Future Atmospheric Nitrogen Deposition, JAS, 73, 2039-2047, 2016.*

*Longo, A. F., Ingall, E. D., Diaz, J. M., Oakes, M., King, L. E., Nenes, A., Mihalopoulos, N., Violaki, K., Avila, A., Benitez-Nelson, C. R., Brandes, J., McNulty, I., and Vine, D. J.: P-NEXFS analysis of aerosol phosphorus delivered to the Mediterranean Sea, Geophys. Res. Lett., 41, 4043–4049, <https://doi.org/10.1002/2014GL060555>, 2014.*

*Im U., S. Christodoulaki, K. Violaki, P. Zarbas, M. Kocak, N. Daskalakis, N. Mihalopoulos and M. Kanakidou, Atmospheric deposition of nitrogen and sulfur over Europe with focus on the Mediterranean and the Black Sea, Atmospheric Environment, 81, 660-670, 2013.*

*Markaki Z., M.D. Loye-Pilot, K. Violaki, L. Benyahya, N. Mihalopoulos, Variability of atmospheric deposition of dissolved nitrogen and phosphorus in the Mediterranean and possible link to the anomalous seawater N/P ratio, Marine Chemistry, Volume 120, Issues 1-4, Pages 187-194, 2010.*

*Theodosi C., Z. Markaki, A. Tselepidis, N. Mihalopoulos, The significance of atmospheric inputs of soluble and particulate major and trace metals to the eastern Mediterranean seawater, Marine Chemistry, Volume 120, Issues 1-4, 20, 154-163, 2010.*

*Theodosi C., Z. Markaki, N. Mihalopoulos, Iron speciation, solubility and temporal variability in wet and dry deposition in the Eastern Mediterranean, Marine Chemistry, Volume 120, Issues 1-4, 20, 100-107, 2010.*

*Guerzoni, S., Molinaroli, E., Rossini, P., Rampazzo, G., Quarantotto, G., and Cristini, S.: Role of desert aerosol in metal fluxes in the Mediterranean area, Chemosphere, 39, 229–246, [https://doi.org/10.1016/S0045-6535\(99\)00105-8](https://doi.org/10.1016/S0045-6535(99)00105-8), 1999.*

*Frau, F., Caboi, R., and Cristini, A.: The impact of Saharan dust on TMs solubility in rainwater in Sardinia, Italy, in: The Impact of Desert Dust Across the Mediterranean, edited by: Guerzoni, S. and Chester, R., Springer, Dordrecht, 11, 285–290, [https://doi.org/10.1007/978-94-017-3354-0\\_28](https://doi.org/10.1007/978-94-017-3354-0_28), 1996.*