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Comment on acp-2021-624

Rachel Shelley (Referee)

Referee comment on "Wet deposition in the remote western and central Mediterranean as a source of trace metals to surface seawater" by Karine Desboeufs et al., Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2021-624-RC1>, 2021

General comments

The manuscript, 'Wet deposition in the remote western and central Mediterranean as a source of trace metals to surface seawater', by Desboeufs et al. presents data on trace metals (TM) in rain and surface water samples. The current title is generic and could be more descriptive such as 'A comparison of two contrasting wet deposition events in the remote western and central Mediterranean and their impact of trace metal behaviour in surface waters.'

The authors present rainwater TM (12 elements), Al, P and N species concentrations and EFs, and discuss these parameters in terms of their fluxes and impacts on concentrations of dissolved and particulate fractions in the upper 20 m of the water column, including the SML. The relatively large number of parameters under discussion results in rather a long paper. Nevertheless, this dataset is the first of its kind for the remote Mediterranean Sea and highlights differences between TM concentrations in rainwater from studies (mainly) in the 1990s conducted at coastal locations. Therefore, this study provides valuable new data from a relatively remote region that is influenced by anthropogenic emissions from Europe, episodically interspersed by pulses of Saharan dust, both of which are delivered to the surface ocean via atmospheric deposition (wet and dry). Wet deposition is thought to have a disproportionately high influence on TMs in surface waters as they are thought to be delivered already in a soluble (and potentially bioaccessible) form. This study illustrates that only some of the TMs studied were delivered predominantly in soluble form; an important point that the authors could emphasise more. Furthermore, rain samples are notoriously challenging to collect at sea. Having paired water column and rain samples is a valuable addition to the scientific literature. I recommend that this manuscript is accepted pending major revisions, given that a restructuring is suggested.

Specific comments

There is no mention of dry deposition – it is important to note that dry deposition is also an important source of TMs.

Specific values from this study are needed in the Results section text. I have made suggestions in the text as to where these would be of value.

I suggest restructuring this manuscript to combine the Results and Discussion sections. This will make this manuscript easier to follow and stop the unnecessary repetition. It would also help to reduce the length of the manuscript.

One of the sticking points for me is the mismatch between SML sampling, ML sampling and rain sampling. I fully appreciate the challenges associated with sampling the SML. Rain, wind speed and sea state all impact the integrity of the SML making it extremely challenging to collect a SML sample immediately prior to and after a wet deposition event. It has been demonstrated that the SML reforms rapidly when wind speed drops below a threshold and that TMs have a short residence time in the SML (minutes to hours, compared to a few days in a 20 m mixed layer). I am concerned that the delay in sampling caused by the meteorological conditions would have missed the TM dynamics in the SML in response to the wet deposition, likely skewing the results towards a higher ratio of dissolved to particulate TMs being observed. The authors note that dissolution of TMs continues after deposition. I think the data is of value but I would like to see some more discussion of the limitations and challenges of sampling the SML at the resolution that would be needed to demonstrate the 'true' impact on TM concentrations following wet deposition. The authors do go some way towards discussing the limitations of the SML sampling towards the end of the manuscript, but I feel it needs to be addressed sooner and in more detail.

I also feel that the significance of these findings is a little overstated as only two rain events were sampled. However, combined with findings from previous studies, it is apparent that the data supports the assertion that wet deposition impacts the mixed layer inventory of TMs. As I mentioned in the General Comments, one of the most interesting findings for me was the relative proportions of dissolved to particulate fractions and how this changed in response to the wet deposition, even with the limitations associated with the SML data.

Line 34. Define DOC

Line 44. ML not yet defined

Line 49. Give examples/define continental aerosol in brackets

Line 52. Biosphere is too general. I suggest replacing it with microbial as it's this community that are directly accessing the dissolved nutrients in seawater

Line 52. State which nutrients

Line 79. I suggest preceding the sentence that starts in this line with 'To the best of our knowledge, ...' as there are studies that have determined concentrations of TMs in rainwater and seawater simultaneously. There are several other studies that have combined rain and seawater concentration data in recent years (e.g. Buck et al., 2010; Shelley et al., 2017) and others that have incorporated wet and dry deposition, combined with seawater concentrations and SML concentrations, although they may not have published their findings yet. What differs with this study is that a suite of elements were determined from the same location, rather than when the ship was underway, in a region of highly variable atmospheric dust inputs where no such data has previously been published. Therefore, I also suggest changing 'reported' to 'published' (line 80) to avoid instances of reporting of unpublished data at conferences or in theses.

Line 95. Possibly more important in terms of why coastal atmospheric TM concentrations might not be representative of open ocean samples is gravitational settling during atmospheric transport. Add a statement to this effect.

Line 109. Delete 'Research Vessel' and remove brackets from around R/V

Line 116. Delete (PC) as you don't use this abbreviation anywhere else in the text

Line 112. Change to 'The rain collector'

Line 126. Reorder this list and restructure this section. The focus of this manuscript is TMs so they should come first. I suggest i) TMs, ii) DOC, iii) major seawater and atmospheric ions, iv) pH. After the list describe the methods for each parameter in the order they are listed. Currently, the list and the methods are mixed together.

Line 144 and 147. Not all analytes are discussed in the manuscript. Please indicate which ones are discussed.

Line 154. More detail needed. I am not clear what the rain blanks were. What were the blanks for the dissolved fraction? Empty bottles swished out with MQ or acidified MQ - one unfiltered aliquot for total wet deposition and a filtered aliquot for the dissolved fraction?

Line 161. Delete: 'For the sample concentration computations, we subtracted these blanks values to elemental concentrations obtained in rain samples.' Replace with 'Blank concentrations were subtracted from all sample concentrations.' State where the analytical figures of merit can be found.

Line 172. '..., detection limit for all analytes was 0.5 ppb, ...'

Line 174. Inconsistent use of date format. Sometimes words - day month, sometimes - month day, sometimes dd/mm. Also include the year in the chosen date format.

Line 198. By rinsing the glass plate with 0.5 L of ultra-pure water – presumably this water was collected as the blank solution? If so, state this.

Line 196. Delete MQ water and replace with $18 \text{ m}\Omega \cdot \text{cm}^{-1}$.

Line 206. Word order – change to: TM samples were also collected in the water column using a titanium trace metal clean (TMC) rosette (mounted with 24 teflon-coated Go-Flo bottles) before and after the rain events (Bressac et al., 2021). Although rosette deployments were performed over the whole water column, we focus here on the 0-20 m mixed-layer (ML)

Line 217. Replace digested with UV-treated.

Line 222. Which metals? Mo and Pb or not all samples were preconcentrated for all metals listed? Reword to make this clearer.

Line 236. Not exactly true but the vast majority of Al is crustal. Therefore, it is currently accepted as one of the best proxy elements. It is predominantly crustal, not only.

Line 239. Reword to: considered significantly enriched, which points to a non-crustal source (Rahn, 1976).

Line 244. Change to wet deposition fluxes.

Line 254 and many other instances. Sometimes you use ship, sometimes R/V, perhaps best to stick with one for consistency.

Line 256. Include equation and explanation for using VWM rainfall.

Line 261. best tool to estimate rainfall in the surroundings of the R/V because...

Line 264. Replace more or less with approximately

Line 267. Integrated rain rates, not integral

Line 271. Replace layer with SML

Line 276. ML, ML depth or MLD – multiple examples throughout the text. Check for consistent use.

Line 286. Is there a reference for this approach?

Line 291 on – Section 3.1. No need to use the word hereafter.

Line 302. Replace surrounding with vicinity

Line 307. Replace rate with volume. Rate requires a time dimension. Word order improvement suggested in edited version of manuscript.

Fig. 1. Format the date consistently. I would like to see Fig. S3 here for comparison rather than it be buried in the Supplementary Material.

Line 337. Reword for clarity. Suggested: The dust plume was concentrated between 3 and 4 km at the beginning of the station occupation, then expanded down to the marine boundary layer (about 500 m amsl) by the end of the day on 3 June 2017. The mass integrated concentration of dust aerosols derived...

Fig. 2. Can you devise another labelling scheme? You have panels a-c and labelling within panel a of arrows a-c, and in panel c of box a-c. All these a-cs get a bit confusing.

Line 355. Change to time then date to make it easier to follow.

Line 367. Repetition. Delete estimates.

Line 368. Delete around

Line 388. What exactly do you mean by stocks? Sometimes it seems to mean concentrations, others partitioning. I think it would be better to replace stocks with partitioning, if that is what is meant.

Line 389. Are you really talking about deep water masses or just water below the ML?

Section 3.3. Values are needed. Please add where indicated in edited version of manuscript.

Line 397. Add concentration of dMo in seawater (~ 107 nM from the reference you cite).

Line 400. Did any of these studies determine pMo and/or dMo? If not, say that your ones are the first

Line 403. Add values of dZn and pZn.

Line 404. How high? Is contamination suspected?

Line 405. The concentrations in the SML were lower than in the ML and Pb dominated both in dissolved and particulate phases. I don't understand, what did Pb dominate?

Fig. 4. Box plots are two words not one. Could the panels be plotted on the same scale to make comparison easier?

Line 418. Med to Mediterranean

Line 424. Reword. The FAST rain concentrations were within the published range, whereas the ION rain was in the low range, confirming a background signature at this station.

Line 426. Define DIN/DIP

Line 428. Bulk deposition – do you mean wet + dry? Clarify.

Line 430. (in the case of DIN/TDP), but averaged about 100 in bulk deposition – state if this was in unfiltered rain. You have switched from talking about DIN/DIP to presenting data for DIN/TRP. Note this.

Line 433. Include range

Line 434. Replace emphasised with observed

Line 436. Add 'the' before Mediterranean. Wrong tense – change have been to were and include value.

- Delete Islands

Fig. 5 caption. Suggested reword: Comparison of dissolved (D) and total (T) TMs concentrations along with data from 14 former studies carried out in to previous studies in the eastern and western Mediterranean Sea.

Line 452. Replace notably with especially

Line 456. Are you comparing like with like here? You state that concentrations likely decrease offshore and, although emissions of TMs may have decreased, if the literature data is from coastal sites you don't have direct evidence for this decline over the open ocean. However, you could infer it from reductions in leaded fuel and coal combustion. Is the decreasing atmospheric input evident in the full depth water column samples? Perhaps this is what the Fu et al data shows but the reader can't check this as the reference is 'in prep'.

Later you mention the Dulac thesis as evidence. This paragraph needs rewriting and making more concise in order to strengthen your final, important statement. As it stands, this section is too speculative.

Line 456. Switch order to Pb and Cd as the impact of a reduction in atmospheric Pb inputs is well documented. You could cite the GEOTRACES IDP as evidence here.

Line 464. Reword: '...related to the decrease in anthropogenic emissions. Thus, our results show the data from before [year] should not be used as a current reference for coastal rain composition due to recent environmental mitigation of TM emissions.'

Line 465. Your rain was open ocean not coastal so doesn't really show that historical coastal TM concentrations are higher. The comparison is with the thesis. You could say that coastal values are not representative of open ocean values in general.

Section 4.1.2. This section jumps around a bit, Rain ION then Rain FAST, the Rain ION again, then both, etc. It would be easier to read if one station was discussed and the other one contrasted to it

Line 468. Define EF here

Line 469. Replace Earth with continental crust

Line 471. Delete slightly. You have stated that TMs with EFs >10 are considered significantly enriched.

Line 474. Reword and clarification needed - For both rain samples, the EF of Zn was on average five times higher than the EF found in rain samples from coastal sites (?) in the Mediterranean region (Özsoy and Örnektekin, 2009; Al-Momani et al., 1998; Losno, 1989). However, extremely high enrichments of Zn in rainwater have been reported from

island sites in the Mediterranean Sea, for example, Frau et al. (1996) reported geometric mean EFs of ~ 6500 in both crust-rich and crust-poor rains from two sites in southern Sardinia, and Fu et al. (2017) reported $EF > 1000$ for Zn in atmospheric bulk deposition on Lampedusa Island. The Zn EF at station ION is the same order of magnitude as at these island sites which suggests... – something about the evidence for an anthropogenic background signal in the open Med.

Was the atmospheric bulk deposition on Lampedusa bulk wet deposition or bulk wet + dry? If so, for clarity best to just say rain. If bulk dry you need to state that too.

Line 485. New paragraph. ‘...particulate TM and P concentrations in seawater have...’

Line 486. Potential local influences - what do you mean here? To resolve the contribution of various local industries and shipping or local inputs from long range transport?

Line 487. As the atmospheric gas and particle measurements do not indicate an anthropogenic influence, you cannot say that the concentration and EF values confirm an anthropogenic influence – your data tells a conflicting story.

Line 497. How does this study compare to the factor of three increase in concentrations between background and dust influenced rains – use your values – and state how this would impact EFs – more AI drives down EFs, AI predominantly from mineral dust, etc.

Line 505. Vague, just say that concentrations were higher and EFs suggest the reason for this was the impact of the dust plume. The EFs don’t really tell us this. This section needs tightening up.

Line 516. Can you suggest a reason for the difference?

Fig. 6. Could you make the two panels the same size and the bars the same width?

Line 525. Could draw parallels with aerosol samples here, e.g. Jickells et al. (2016)

Line 535. Dust loading is only one proposed control and may not be a direct control – provide explanation e.g. perhaps the $CaCO_3$ concentration is or the reduced impact of acidic gases, relative humidity, etc. – ref Baker et al., 2021.

Line 538. Therefore, your data does not support this argument. Disagreement within statement. The EFs close to crustal TMs in RainFAST combined with the higher concentrations point to the role of mineral dust in reducing the fractional solubility of TMs in rainwater – or the presence of mineral dust overwhelms the background signal resulting in a net decrease in fractional solubility – although the net effect is the same, I favour the latter explanation.

Line 540. Mo has a high concentration in SW. If it has a predominantly marine source this could explain your uniform solubility. It would not explain your increase in EF necessarily but if there was an increase in seasalt aerosols it could do. You have the data to test this hypothesis. How reliable was the Mo solubility data? How close to LoD and blanks?

Line 551. How large?

Line 566. This is different than the Al percentage used in your EF calculations (~ 8% Rudnick and Gao, 2003). Your EFs would be lower if you used concentrations based on 7.1% Al (Guieu et al., 2002) or your fluxes would be higher if you used the Rudnick and Gao %. It would be worth noting this variability. There is certainly an argument for using Saharan elemental ratios in your EF calcs (as discussed in Shelley et al., 2105).

Line 563. Fluxes aren't measured directly so reported, calculated or estimated are better words.

Line 565. Reword: The aerosol columnar concentration during the dust event was estimated to be between...

Line 566. This is x3-4 higher than your flux estimates. A sentence to clarify why you support this view.

Fig. 7 caption. Add 'Note different scales on the y axes.'

Fig. 7. It would be useful to see the Al wet deposition flux as this is what you are using as the basis to estimate the bulk wet deposition fluxes. It would also be nice to have a third panel showing the ratio of dissolved to particulate TMs – or Kds.

Line 579. Explain how these two parameters differ. Are they not the same thing in the

context of this work?

Line 579. Explain why. They (Co, Cd, Mo) also have the greatest uncertainties – low concentrations and high blank contributions

Line 583. Because these elements (Cr and Ti) were primarily found in the particulate phase?

Line 584. Emphasised is stretching it for data from just two samples

Line 586. With the exception of Mn, these are predominantly considered pollution derived elements. It would be worth mentioning this.

Line 587. Poorly soluble, lithogenic elements. Al should also be reported here. I'm assuming it showed the same behaviour as Fe and Ti?

Line 596. Do you mean the orders of magnitude range? Say how many orders of magnitude.

Line 590. What does 'dust-related elements' mean? All elements discussed or only lithogenic elements?

Section 4.2.2. I'm wondering if concentrations or partitioning are better words than stocks (this applies throughout the paper).

Line 594-597. Move to Methods.

Fig. 8. Move to methods.

Fig. 8 caption. Given how quickly the SML TM concentrations respond to atmospheric inputs and their relatively short residence times in the SML (mins - hours in Ebling and Landing, 2015), how can you be sure that your SML sampling resolution was capturing the impact of the wet deposition events on the SML, especially given that wind speed (and sea state) is a critical factor in determining the integrity of the SML?

Line 614. As it reforms so quickly and rain disrupts it, how can you be sure that the SML sampled after the rain at FAST was in contact with the atmosphere and accumulating TMs from wet deposition?

Line 616. Suggesting that there was a surface advective current?

Line 619. Dissolved or particulate or both?

Line 623. I wonder if this is because of the mismatch between SML sampling and rosette casts.

Line 629. Additional to what?

Line 630. The particles could also be scavenging dissolved TMs

Line 632. Again, the SML samples may not be representative of the wet depo inputs. In contrast, the ML likely was

Line 648. If we assume that the SML samples were representative of this layer before and after rain (and even if we don't), the similarity in Mo concentrations suggests to me that this element is not primarily delivered by atmospheric inputs

Line 651. From rain or total (wet + dry) atmospheric depo?

Line 653. Days?

Line 655. Some ML residence time calculations could be of use here

Line 661. Many people have shown a delayed response of the dissolved pool to atmospheric inputs and hypothesised why there is a lag.

Line 671. It would be useful to see this – put in Supplementary Material.

Line 677. New paragraph.

Line 671. I'm not completely convinced it does because of the resolution problem. It certainly suggests it might given Tovar-Sanchez's findings of increases 24 h after rain but the signal is likely to be (significantly) diminished after this time.

Line 686. Delete 'at the scale' and replace with 'in the'

Line 704. Which ones? Theodosi reports this for the TMs he studied but not your full suite. There are some that do, some that don't. See Jickells et al., 2016 and Baker et al., 2020. I appreciate these papers report data for the Atlantic rather than the Med but as they report data from Saharan and European air masses they are relevant.

Line 734. Only dissolved or dissolved and particulate?

Line 752. How about an extra statement suggesting additional dry deposition sampling to directly compare the inputs of wet and dry deposition in future? The contribution of dry deposition seems to have been overlooked in this study, in the sense that there is no comment about the contribution of dry deposition. What is thought to be the relative contribution of wet-dry dust deposition events in the Med. Is wet deposition thought to have a disproportionately large impact on TM seawater concentrations during stratification?

Technical corrections

There are many examples of incorrect agreements and syntax. I have attempted to catch them but may have missed a few. For the most part, these small errors do not impact too much on the readability of this manuscript, but it would be greatly improved by correcting them. I have included an edited version of the manuscript to help identify where these occur as they are too numerous to include in this review.

It seems unnecessary to use the Med Sea abbreviation as it is used inconsistently throughout the manuscript.

Trace metal or trace element? You switch part way through.

Additional references

Baker, A.R. et al. 2021. Changing atmospheric acidity as a modulator of nutrient deposition and ocean biogeochemistry. *Science Advances* 7: eabd8800. Doi: 10.1126/sciadv.abd8800; **Baker, A.R. et al.** 2020. Trace Metal Fractional Solubility in Size-Segregated Aerosols From the Tropical Eastern Atlantic Ocean. *GBC*. 34: e2019GB006510. Doi, 10.1029/2019GB006510; **Buck, C.S.** et al. 2010. The solubility and deposition of aerosol Fe and other trace elements in the North Atlantic Ocean: Observations from the A16N CLIVAR/CO₂ repeat hydrography section." *Mar. Chem.* 120: 57-70; **Ebling, A.M. and Landing, W.M.** 2015. Sampling and analysis of the sea surface microlayer for dissolved and particulate trace elements. *Mar. Chem.* 177: 134-142; **Jickells et al.** 2016. Atmospheric transport of trace elements and nutrients to the oceans. *Phil. Trans. Royal Soc. A.* 374. Doi: 10.1098/rsta.2015.0286; **Shelley, R.U. et al.** 2015. Elemental ratios and enrichment factors in aerosols from the US-GEOTRACES North Atlantic transects. *DSR II*. 116: 262-272. Doi: 10.1016/j.dsr2.2014.12.005; **Shelley, R.U.** et al. 2017. Quantification of trace element atmospheric deposition fluxes to the Atlantic Ocean (> 40°N; GEOVIDE, GEOTRACES GA01) during spring 2014. *DSR I*. 119: 34-49. Doi. 10.1016/j.dsr.2016.11.010.

Please also note the supplement to this comment:

<https://acp.copernicus.org/preprints/acp-2021-624/acp-2021-624-RC1-supplement.pdf>