

Interactive comment on “Phosphorus solubility in aerosol particles related to particle sources and atmospheric acidification in Asian continental outflow” by Jinhui Shi et al.

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Responses to Reviewer 2# Comments

Reviewer #2 (Comments to Author):

The manuscript investigated the P speciation and solubility in aerosols in the eastern China's coast. Phosphorus may ultimately control the primary production in the large areas of the ocean especially in the N-affluent regions such as the marginal seas of the western North Pacific. The previously reported P solubility in aerosols was in a wide range, and therefore it is important to understand the factors or mechanisms

C1

determining the atmospheric input of soluble P. The manuscript studied the coordinated effect of relative humidity (RH) and aerosol origins and acidity on P solubility, and also included dissolved organic P in the discussion. The manuscript indicated that P in aerosols from anthropogenic sources had a higher solubility than the P in aerosols from mineral dust. Phosphorus solubility was usually less than 30% when the RH was below 60% and the higher RH increased the dissolution of aerosol P to a great degree under acidic conditions (how to define acidic condition?). These results will be very helpful to modeling the input of bioavailable P to the ocean. It would be nice if authors could discuss extrapolation of the results to the eastern China seas, other coastal regions or even the open ocean.

Response: We thank the reviewer for the careful evaluation and helpful comments to improve the quality of our manuscript. We revised the manuscript and addressed the reviewer's comments.

The acidic condition here is a relative value. We define it with respect to the average acidification degree of all samples.

We found that the P solubility and the Al concentration (as dust loading) displayed an inverse power-law relation (Section 3.3.1). Literature data from the eastern China sea areas also show similar relations between P solubility and mineral contents in aerosols. In the revision, we added “These results indicate the potential to extrapolate the discussion of this study to the seas to eastern China.” on Page 9, Line 10.

Introduction Page 2 Line 3: Authors may add few sentences on the importance of atmospheric P deposition to the surface ocean. For example, long-term measurements of dissolved P at station ALOHA revealed unexpected temporal variability in PO₄³⁻ concentrations in the surface ocean, which may be partly due to the episodic atmospheric deposition (Karl and Tien 1997). Karl DM, Tien G. 1997. Temporal variability in dissolved phosphorus concentrations in the subtropical North Pacific Ocean. *Mar. Chem.* 56:77–96

C2

Response: In the revised version, we added “Atmospheric P deposition likely has an important contribution to phosphate and induces the growth of phytoplankton in surface seawater outside estuary areas, especially in offshore areas and regions where P limits phytoplankton growth (Karl and Tien, 1997; Paytan and McLaughlin, 2007; Mackey et al., 2012a).” in the Introduction (Page 2, Lines 4-6).

Methods Page 4 Line 26, “P” at the beginning of the sentence should be changed to “Phosphorus”

Response: Revised as suggested.

Page 5 Line 18: “because P is a substance in primary particles”. Here what is the general size range for primary particles? Authors may provide the reference or the size distributions of P and DP to prove the statement. Page 5 line 18-20: “In cases when the samples contained less mineral dust, the aerosol mass would be somewhat underestimated.” The mass loadings estimated from Al concentrations may be compared to the officially reported PM10 concentrations to check for the average underestimation.

Response: The description of “because P is a substance in primary particles” in the original manuscript was changed to “because more than 90% of TP is in the $>0.32 \mu\text{m}$ particles (Vicars et al., 2010)”. Vicars et al (2010) was cited to support our statement. (Page 5, Line 23)

Vicars, W. C., Sickman, J. O., and Ziemann, P. J.: Atmospheric phosphorus deposition at a montane site: Size distribution, effects of wildfire, and ecological implications, *Atmos. Environ.*, 44, 2813–2821, 2010.

The official PM10 data were available only after December 2013. We have a small number of filter-based TSP data, and they show a quite good correlation with the Al-based estimation. To avoid confusion, we deleted this sentence in the revision.

Results and Discussion Page 6 Line 3-5: The two sentences can be combined to be more concise.

C3

Response: The two sentences have been combined to “DIP and DOP accounted, on average, for approximately 60 % and 40% of the TDP, respectively, indicating an appreciable contribution of DOP to the TDP.” Please see Page 6, Lines 7-8.

Page 6 Line 27: “This result was probably caused by the release of primary biological particles and agriculture fertilization in spring.” Was DOP released by the agricultural process in spring or as the loss of fertilizer (I thought that fertilizer should be mainly DIP)?

Response: Agricultural insecticides is one of sources of OP in atmospheric aerosols (Kanakidou et al., 2012). The description “agricultural fertilization” is inaccurate in the original manuscript, we replaced it with “agricultural activities” (Page 6, Line 30).

Page 8 Line 18: The statement “a small fraction of biological P” needs to be supported by a reference or observatory data.

Response: Wang et al. (2015) estimated combustion-related emissions of 1.8 Tg P yr⁻¹, which represent over 50% of global atmospheric sources of P (3.5 Tg P yr⁻¹), and the primary biogenic particles emission is 0.58 Tg P yr⁻¹ to contribute 17% of the total P emission. We cited this reference to support our statement (Page 8, Line 23).

Wang, R., Balkanski, Y., Boucher, O., Ciaïis, P., Penuelas, J., and Tao, S.: Significant contribution of combustion-related emissions to the atmospheric phosphorus budget, *Nat. Geosci.*, 8, 48–54, 2015.

Page 8 Line 29-31: Why is the correlation of TDP vs soluble Al better than that of TP vs Al? Such comparison is hard to explain. Authors may delete this sentence and just compare the ratios of P/Al to the ratios of TDP/soluble Al.

Response: We deleted this sentence as suggested.

Page 9 Line 31: “Some data points deviated from the fitting curves.” The specific variables for fitting curves should be indicated here, e.g. for P solubility and total Al.

C4

Response: We added the information of the specific variables in the revision. This sentence was revised as “Some data points, for P solubility against total Al and the specific surface area, deviated from the fitting curves (Fig. 4, Fig. 5),” (Page 10, Lines 3-4)

Page 10 Line 11-13 & 18-20: There is repetition in these sentences.

Response: The sentence repeated on Page 10 Line 11-13 in the previous manuscript have been revised to “Following Hsu et al. (2014) who used the ratio of acids/total Fe to investigate the influence of aerosol acidification on the Fe solubility, we use the ratio of acids/total P to investigate the influence of aerosol acidification on the P solubility.” Please see Page 10, Lines 16-17.

The two sentences with repetition on Page 10 Line 18-20 in the original manuscript were revised to “However, the P solubility versus the acid/TP ratio followed different regression curves corresponding to the ranges of Panth/TP, e.g., the slope of 0.22 in samples with Panth/TP > 70 %, while of 0.01 in samples with Panth/TP < 50 %.” Please see Page 10, Lines 22-24.

Page 11 Line 6: “had a statistically significant correlation” What are the variables?

Response: We added the information of the variables. This sentence was revised as “The data points of P solubility against acids/total P for the samples of 50 % < Panth/TP < 70 % were frequently between the two fitted curves of Panth/TP > 70 % and Panth/TP < 50 % (Fig. 6), and had a statistically significant correlation at 99 % confidence ($r = 0.383$, $p = 0.006$).” (Page 11, Lines 11-13)

Page 11 Line 17-32: The coordinate effect could be arranged as another section. The relationships between P solubility and humidity, anthropogenic percentage and acidification are complex. The two paragraphs seem to talk about the situations at RH<60% and RH>60% respectively. But the RH change from <60% to >60% was discussed again in the second paragraph. This part needs to be reorganized.

C5

Response: The first paragraph of Section 3.3.3 demonstrates the effect of relative humidity on P solubility, and the latter two paragraphs demonstrate the coordinate effect of relative humidity and atmospheric acidification. In the revised version, we changed the title of this section to “Relative humidity and coordinate effect of aerosol sources and acidity”. (Page 11, Line 10)

We discuss P solubility corresponding to aerosol sources and acidity at relative humidity < 60% and > 60%, respectively. In the part associated with relative humidity > 60%, we compared the changes of P solubility with the relative humidity corresponding to aerosol sources and acidities. The discussion of relative humidity from <60% to >60% is remained in the manuscript because we effort to compare the increase of the P solubility when the relative humidity was > 60% with that when the relative humidity was < 60%.

Page 11 Line 25: The unit of acidification degree should be unified in the paper. Is it proper to choose 150 acidification degree as the boundary?

Response: The unit of acidification degree was unified in the revised version.

The acidification degree of 150 nmol nmol⁻¹ was close to the average acidification degree of all aerosol samples. We chose this value as the boundary to demonstrate the difference between the two groups of samples above and below the average acidification degree.

Page 12 Line 1-2: The first half sentence talked about the effect of RH on P solubility, and the second half mentioned acidification. The linkage between the RH and acidification was missing.

Response: This sentence has been revised as “Overall, the enhancement of P solubility by RH increase in the mineral aerosols was much lower than in the anthropogenic aerosols, in which P was more susceptible to acidification, e.g., at RH>60%.”. Please see Page 12 Lines 6-7.

C6

Conclusion Page 12 Line 12: “. . . .from mineral dust and anthropogenic sources” can be deleted.

Response: Revised as suggested.

Page 12 Line 17: “The threshold RH for this effect was approximately 60%.” can be deleted.

Response: Revised as suggested.

Please also note the supplement to this comment:

<https://www.atmos-chem-phys-discuss.net/acp-2018-892/acp-2018-892-AC2-supplement.pdf>

Interactive comment on Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2018-892>, 2018.