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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Factors determining the formation of secondary inorganic aerosol: a case study in the Po Valley (Italy)" *by* S. Squizzato et al.

Anonymous Referee #1

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This manuscript synthesizes measurements of inorganic ions and gas-phase species with simple meteorological variables to characterize air pollution in the Po Valley. The strength of the study lies in the incluion of multiple measurement sites over many seasons (albeit with measurement artifacts), but the analysis and discussion should be revised to make the manuscript more relevant and useful. Comments are as follows:

Section 3.2

What was the duration of sampling for each filter?

Section 3.4

How does quartz filters minimize artifacts?

Section 4.2

"multifold" increases have not been observed in atmospheric conditions or conditions mimicking atmospheric concentrations (Iinuma et al., 2004). The work by Jang et al. (2002) claiming multifold increases were reported under concentration domains exceeding ambient conditions.

Section 4.3

D_link and D_max appears not to have been defined. How was the 25% threshold determined?

Aerosol acidity has traditionally been characterized by the terms, strong and free acidity (e.g., Saxena et al. 1993, Koutrakis and co-workers, etc.) rather than total and in-situ acidity. Why have the authors chosen these terms? The authors also refer to the [H+]_Total as strong acidity.

The analysis and discussion of ammonium nitrate formation does not add much content to the scientific literature. The main conclusions are that conditions which favor ammonium nitrate formation occur when there is ammonia in excess of that required to (partially) neutralize sulfate, temperatures are low, and RH is high. But this has been known for some time. The use of excess ammonia, NR, and ratios of NO3- and NH4+ to nssSO4 all express a similar phenomenon; this excess is related to the NO3- in the particle phase. The point of this analysis is not clear. Similarly, Figure 3 makes a rather obvious statement. What is the usefulness in including this figure? Do the regression lines have any relevance? Why is there more scatter in the SRC points?

Section 4.4

Is it correct to call these oxidation ratios, since they are calculated only the aerosol fraction and not total (gas+aerosol) HNO3 or H2SO4? (So these are not really measures of oxidation, per se).

How can the correlation with PM2.5 and NO3- be so high when the nitrate fraction is

ACPD

12, C6354–C6356, 2012

about 25% on average (even if ammonium contributing to PM is added on top of that) from Fig. 2? And why would it be different from nssSO4. The local/non-local argument is not clear.

Conclusions

In general, it is not clear what is the "approach" that can be adapted elsewhere?

I think the finding that the strong acidity being lower than in China but the free to strong acidity ratio being similar is a relevant finding.

Regarding Sections 4.3 and 4.4, the results of the cluster analyses are lacking discussion, especially regarding their relevance. E.g., low windspeeds = stagnant conditions and how much of a role this plays beyond temperature and humidity in regulating PM2.5 concentrations. The airmass predominantly comes from the northeast; the periods in which come from the southeast (ocean) must have a different composition but why are they clustered with the ones coming from the northeast? There should be a direct comparison between the two clustering approaches used in section 4.3 and 4.4 and how using different variables (e.g., inclusion of gas-phase species) or transformation on variables leads to characterization of different air "pollution" regimes. I think the most interesting statement regarding the main contributing inorganic compounds to PM2.5 by season and airmass origin can be made without a cluster analysis, though cluster analysis can be used to aid the discussion. As partially stated above, Tables 3 and 4 can be made into a figure combined with Figure 4.

Interactive comment on Atmos. Chem. Phys. Discuss., 12, 16377, 2012.