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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 #2

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General comments:

The manuscript describes the contribution of secondary inorganic aerosol to PM2.5 in the eastern Po Valley. The data presented are valuable; they have been collected at three different sites (urban background, industrial, and semirural coastal sites) during long-term campaigns for a period longer than three years.

Data presented in the paper helps to describe PM level and composition in one of the most polluted areas of Europe and aims at improving knowledge on the effects of meteorological parameters and trace gas concentration on aerosol formation and properties. In this context, the manuscript need minor revision in order to pinpoint this objective more clearly.

The conclusions concerning regional and local sources of nitrate and sulfate need to be supported by stronger evidences. The attribution of sulfate to regional sources is based on the time trend of non-sea salt sulfate (lack of seasonality), and to the unexpected higher sulfur oxidation rate (SOR) during the colder (less photochemical active) season.

Specific comments:

Section 3.4 "Sampling possible artifacts": The authors should specify if the average nitrate loss percentages refer to the entire dataset or refer to the subset of samples potentially affected by sampling artifacts (95 out of 445). The authors should also explain how the samples potentially affected by artifacts are treated in the following part of the paper, and thus how these artifacts might affect the acidity results.

Section 4.2 "Aerosol acidity": The average values do not look statistically different from 1. Probably the reader would be helped in interpreting acidity results by a more comprehensive discussion of pH and [H]ins+ values at the light of literature data. Are pH results comparable to values reported for other urban areas in Europe? Or acidity is closer to what observed in industrialized areas? What are the potential consequences of higher aerosol acidity in summer in term of heterogeneous phase chemistry?

Section 4.3 "Ammonium nitrate formation": the authors could support the conclusions relative to the effect of meteorological conditions on ammonium nitrate formation adding average meteorological parameters for each cluster in table 3.

Section 4.4 " Sulfur and nitrogen oxidation ratios": Previous studies showed that SOR is higher in summer due to higher atmospheric photochemical activity (Wang et al. 2005), while the authors obtained different seasonal trends for the investigated sites, i.e. higher SOR in winter. As a consequence the authors did not observe a correlation between SOR and temperature as observed in previous studies. These results are used to attribute sulfate to regional sources. This conclusion should be stronger supported, for example by discussing regional emission inventories, if available, and

comparing SO2 and sulfate concentration with other urban and industrial areas. The vicinity of a petrochemical area makes necessary discussion and analysis of other significant regional sources of sulfate, before excluding the local origin.

Technical corrections:

Abstract Line 9 and 11: It would be helpful to specify the meaning of acronyms (E-AIM and SIA) in the abstract and then in the text, the first time they are mentioned.

Line 19: probably the author meant “weather conditions” rather than “climatic conditions”.

Introduction

Page 16379

Line 5: “chemical reactions and physical processes” instead of “chemical reactions”

Line 10: “Secondary Inorganic Aerosol (SIA)” instead of “SIA”

Line 24: In Europe, even when 95% of the total mass. . .

Line 25: coarse mode (particles with aerodynamic diameter smaller than 2.5 μm)

Line 29: the secondary aerosols, and locally marine components,. . .

Page 16380

Line 25: the authors should specify the meaning of acronym E-AIM

Page 16381

Line 19: the authors should specify the meaning of acronym ISPRA

Line 22: consistency is advisable when using formulae or name to indicate trace gases

Material and methods:

Page 16382

Geographical coordinates would help the reader to identify sampling site locations.

Line 4: upwind of

Line 12: automated samplers

Line 13: please specify if samples were collected daily (24 hour collection period)

Page 16383

Line 1: and assuming that Na+ was dominated by sea salt emissions.

Page 16384

Line 8: A preferable title could be “potential sampling artifacts”

Line 18: over absorption

Line 25: temperature below 20

Results and discussions:

Page 16385

Line 18: SO2 instead of SOx

Page 16387

Line 11: it affects acidity-dependent heterogeneous chemistry on the aerosol surface. . .

Line 17: NR was used. . .

Page 16388

Line 4:Chinese cities reported in literature and the level. . .

Page 16389

Line 20: “Stoichiometric excess ammonium is defined as” instead of “On the basis of

these results, it is possible to define the excess ammonium as”

Line 23: Nitrate concentration increases when excess NH4 is larger than 1 with a 1:1 ratio. . ..

Page 16390

Line 2: Sulfur oxidation ratio. . .

Line 5 and 6: please define n in the formulae.

Line 7: the authors should add references to specify why the value 0.1 is taken as a threshold that indicates SO2 photochemical oxidation

Figures and Tables

Table 1: Since aerosol acidity is discussed before NOR and SOR, Table 1 readability would improve if the last three rows could be moved before SOR line.

Table 4: Specify why SRC site is not reported in the Table.

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