Answer to Anonymous Referee #2

The authors are grateful to the referee for the comments on the paper which certainly lead to a more profound discussion of the results.
All proposed objections and suggestions have been taken into account and discussed.
The referee’s comments are highlighted in italic font, whereas authors’ replies are in normal text. Added and/or modified sentences are reported within quotation marks (“”).

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 introduction paragraph has been modified to better explain the purpose.

“In this study an approach is proposed to easily interpret aerosol formation processes and acidity properties, using chemical experimental data (ion and gaseous precursors concentrations), readily available meteorological information and a thermodynamic model. At first, aerosol acidity was modeled using the recently released thermodynamic model E-AIM4 (Extended Aerosol Thermodynamics Model). Afterwards, the sulfate-nitrate-ammonium system and the subsequent SIA generation processes have been investigated by a chemometric procedure. Experimental $[NH_4^+]/[SO_4^{2-}]$ molar ratios and NO_3^- concentrations have been tested to explain the environmental and chemical conditions favoring the ammonium nitrate formation. Finally, experimental ion data were examined in relation to the levels of gaseous precursors of SIA (SO_2, NO_x, NO, NO_2) and considering some environmental conditions having effects on SIA generation processes.”

[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).]
Only summer samples with average daily temperatures ≥ 20°C.
This information has been added in the section 3.4

[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.]

Some sentences have been added.
Potential sampling artifacts
"A one-way ANOVA has been performed to compare raw data and data corrected for aerosol nitrate loss. Results showed no significant difference (p-value = 0.916). Both the cluster analysis discussed and an aerosol acidity calculation have been done on raw data and then repeated on corrected data to control artifact effects, but no significant difference has been observed in terms of seasonal mean and standard deviation."

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?]
An extended literature search was made to find comparable data from other European areas. Unfortunately we found no recent study to compare, except the already mentioned data relating to Chinese cities.

[What are the potential consequences of higher aerosol acidity in summer in term of heterogeneous phase chemistry?]
Aerosol acidity can lead to an enhancement in SOA mass concentrations related to acid-catalyzed particle-phase reactions (Surrat et al., 2007; Zhang et al., 2007). Liu et al. (1996) have observed an increase in photochemical activity for higher aerosol acidity, $[H^+] > 300$ nmol m^{-3}, during the summer period. A comparison between this data and our data is reported in line section 4.2.
"In summer, higher aerosol acidity, exceeding 300 nmol m^{-3}, can lead to an enhancement in photochemical activity (Liu et al., 1996). However, the observed average aerosol acidity was largely below this limit (max $[H^+]_{strong} = 174.3$ nmol m^{-3}). On this basis, the measured aerosol acidity characteristics cannot lead to serious atmospheric implication."

[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.]
Average meteorological parameters for each cluster have been added 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.]

A discussion about this point has been added in paragraph 4.4.

The Discussion part has been extended as it follows:

"SOR values were higher than 0.1 both in UBG and IND (table 1) showing that SO_2 is photochemically oxidized in the atmosphere (Bencs et al., 2008; Ohta and Okita, 1990). The highest SOR values were observed during autumn and winter in IND. This may be due to specific sampling site characteristics (closeness to a sulfur emitting coal power plant) and to long range transport processes carrying secondary SO_4^{2-} (Squizzato et al., 2012). The highest NOR values were observed in spring and winter due to favorable conditions (low temperature and high relative humidity) for gas-to-particle conversion processes, in particular for ammonium nitrate formation.

In Veneto, the main emission facilities of SO_2 are represented by mineral oil and gas refineries (39.9%), manufacture of glass (32.5%) and thermal power stations and other combustion installations (22.9%) (E-PRTR, 2012). Most of these activities are localized in Venice, where 59% of SO_2 emission have been estimated deriving from energy production (ISPRA, 2012). Despite this, the levels of SO_2 and sulfate are not so higher than in other urban and industrial areas in the Veneto region and in Europe. In table 4 a comparison is reported between SO_2 and sulfate concentration detected in this study and in other areas. Compared with European studies, the levels of sulfate are similar, but the SO_2 concentrations are generally lower than those observed in other studies.

Wang et al. (2005) observed a positive correlation between SOR and temperature. This suggests a possible oxidation mechanism of SO_2 to SO_4^{2-}, because the local gas phase oxidation of SO_2 by OH radical, followed by the condensation or absorption into the particle phase is a strong function of temperature (Seinfeld and Pandis, 2006). In this study, lower correlation coefficients were observed ($r< 0.5$) between $PM_{2.5}$, SO_4^{2-}, SO_2, NH_4^+ and SOR and between SOR and temperature. Conversely, a negative correlation between temperature and NOR ($r=-0.5$) has been observed, suggesting a local gas phase oxidation. Moreover, $PM_{2.5}$ concentrations are strongly correlated with NO_3^- ($r= 0.9$), NH_4^+ ($r= 0.9$), NO_2 ($r= 0.7$) and NOR ($r= 0.8$). On this basis, nitrate formation can occur at a local level, whereas SO_4^{2-} may depends on regional contributions."

Table 4. Comparison between SO_2 and sulfate concentration detected in this study and in other areas.

Location	**Site type**	**Sampling period (from-to)**	**Compound**	**Average concentration (ug/m3)**	**Reference**
Venice - UBG	Urban background	all sample	Sulfate-SO_2	3.3-3.7	this study
Venice - IND	Industrial	all sample	Sulfate-SO_2	3.6-5.6	
Venice - SRC	Rural background	all sample	Sulfate	3.5	
Flanders, Belgium	Industrial	19/12/2002-23/02/2003	Sulfate-SO_2	2.7 - 34	Bencs et al., 2008
	Urban	10/02/2003-07/04/2003	Sulfate-SO_2	4.3 - 18	
	Suburban	11/12/2001-30/01/2002	Sulfate-SO_2	4.5 - 19	
	Rural	27/02/2002-15/05/2002	Sulfate	0.8	
Elche, Spain	Urban backgorund	October 2003-September 2004	Sulfate	4.3 (in PM_{10}) 3.3 (in $PM_{2.5}$)	Galindo et al., 2008

Thessaloniki, Greece	Urban	July 1997–July 1998	Sulfate	4.8	Tsitouridou et al., 2003
	Urban/Industrial	July 1997–July 1998	Sulfate	7.2	
	Residential	July 1997–July 1998	Sulfate	7.2	
Istanbul, Turkey		2002-2010	SO_2	16.6 (EU side) 10.9 (Asian side)	Ozcan, 2012
Veneto cities					
Padova	Urban backgorund	29/01/10 -01/03/10, 22/07/10 - 23/08/10	SO_2	1	ARPAV, 2012
Verona	Traffic	Full year - 2010	SO_2	3	
Belluno	Urban backgorund	Full year - 2011	Sulfate-SO_2	2.2 [a] - 1	
Vicenza	Traffic	Full year - 2011	SO_2	1	
Treviso	Urban background	Full year –2011	Sulfate-SO_2	3.1 [a] -4 [b]	

[a] sulfate concentration values have been provided by ARPAV – Regional Service Laboratories

[b] SO_2 concentration values have been provided by ARPAV – Department of Treviso

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.]
Done

[Line 19: probably the author meant “weather conditions” rather than “climatic conditions”.]
Climatic conditions have been changed in weather conditions.
[Introduction]
Page 16379
Line 5: “chemical reactions and physical processes” instead of “chemical reactions”
Done
Line 10: “Secondary Inorganic Aerosol (SIA)” instead of “SIA”
Done
Line 24: In Europe, even when 95% of the total mass
Done
Line 25: coarse mode (particles with aerodynamic diameter smaller than 2.5 µm)
This sentence has been modified: “coarse mode (particles with aerodynamic diameter larger than 2.5 µm)”.
Line 29: the secondary aerosols, and locally marine components,
Done
Page 16380
Line 25: the authors should specify the meaning of acronym E-AIM
Done
Page 16381
Line 19: the authors should specify the meaning of acronym ISPRA
Done

Line 22: consistency is advisable when using formulae or name to indicate trace gases
“Nitrogen oxides” have been changed in NO_x

[Material and methods:]
Page 16382
Geographical coordinates would help the reader to identify sampling site locations.
Geographical coordinates have been added for each sampling site.
Line 4: upwind of
Done
Line 12: automated samplers
Done
Line 13: please specify if samples were collected daily (24 hour collection period)
Done
Page 16383
Line 1: and assuming that Na+ was dominated by sea salt emissions.
Done
Page 16384
Line 8: A preferable title could be “potential sampling artifacts”
The title “Sampling possible artifact” has been changed in “Potential sampling artifacts”
Line 18: over absorption
Done
Line 25: temperature below 20
Done

[Results and discussions:]
Page 16385
Line 18: SO_2 instead of SOx
Done
Page 16387
Line 11: it affects acidity-dependent heterogeneous chemistry on the aerosol surface
Done
Line 17: NR was used
Done
Page 16388
Line 4: Chinese cities reported in literature and the level
Done
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”
The sentence has been corrected.
Line 23: Nitrate concentration increases when excess NH4 is larger than 1 with a 1:1 Ratio
The sentence has been corrected.
Page 16390
Line 2: Sulfur oxidation ratio
Done
Line 5 and 6: please define n in the formulae.
The formulae have been rewritten and better commented.
Line 7: the authors should add references to specify why the value 0.1 is taken as a

threshold that indicates SO2 photochemical oxidation
References have been added.

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