Answer to Anonymous Referee #1

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 (“”).

*[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 inclusion 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?]*
The sampling duration has been added.
Line… : “Sampling time was 24-h, from 0:00 to 24:00.”

*Section 3.4*
*[How does quartz filters minimize artifacts?]*
Some considerations about quartz filter have been added.
Line…: “Teflon filters are characterized by evaporation losses of ammonium nitrate even at low temperature, whereas quartz filters show a good retention up to 20°C (Shaap et al., 2004). Considering the average environmental temperatures of the study area, quartz filters have been used in the sampling campaign to 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.*

In agreement with the referee, the sentence related to this citation has been deleted and replaced with:
“In fact, laboratory observations of enhancement in SOA mass concentrations related to an increase in acidity of inorganic seed aerosol, suggest the presence of acid-catalyzed particle-phase reactions (Surrat et al., 2007; Zhang et al., 2007).”

*Section 4.3*
*D_link and D_max appears not to have been defined. How was the 25% threshold determined?*
“The 25% threshold has been chosen among other cut-off levels, because it permitted to discriminate three groups statistically different from the one-way ANOVA ($p$-value < 0.05).”

*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.*
In the works of Pathak et al., 2004 and Pathak et al., 2009, the terms are equivalent, but considering the referee observation and the suggested articles the terms have been changed.

*[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.]*

As described in the paragraph 1 “Introduction”, ammonium nitrate formation was usually investigated using chemical equilibrium models mainly addressed to understand the partitioning between the gas and aerosol phases. Moreover, other cited studies have highlighted an increase of $NO_3^-$ concentration for $[NH_4^+]/[SO_4^{2-}]>1.5$, but this ratio is referred to different environmental conditions from our sampling conditions.
In this study an easy method is proposed to investigate the sulfate-nitrate-ammonium system and the subsequent SIA generation processes, identifying the $[NH_4^+]/[SO_4^{2-}]$ ratio related to the sampling conditions.
The proposed approach can also be easily applied to other environments to evaluate the physicochemical characteristics of aerosols and the weather conditions necessary for the formation of ammonium sulfate and ammonium nitrate aerosols.
The purpose of this method has been better specified in paragraph 4.3

*[Similarly, Figure 3 makes a rather obvious statement. What is the usefulness in including this figure?]*

To highlight the increment of $NO_3^-$ for $[NH_4^+]/[SO_4^{2-}]>2$.

*Do the regression lines have any relevance?*

The lines are not significant and were eliminated.

*[Why is there more scatter in the SRC points?]*
This site has been chosen for the distance from direct emissions sources. The larger scattering can be due to this feature that makes the site very different from the other two.

*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).*

Correct observation. Nevertheless, SOR and NOR are useful tools to evaluate the degree of atmospheric conversion of $SO_2$ and $NO_2$ based on readily available data like those from networks of air quality.
These considerations have been added at line

“SOR and NOR consider only the aerosol fraction and not the total (gas+aerosol) $HNO_3$ or $H_2SO_4$. Nevertheless, these oxidation ratios represent an useful tool to evaluate the degree of atmospheric conversion of $SO_2$ and $NO_2$ based on readily available data such as those from air quality networks.”

*[How can the correlation with PM2.5 and NO3- be so high when the nitrate fraction is 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 correlation coefficient r is a measure of the correlation (linear dependence) between two variables *X* and *Y*, giving a value between +1 and −1. It is widely used in the sciences as a measure of the strength of linear dependence between two variables and it does not depend on the size of the variable.

*[The local/non-local argument is not clear.]*
As also suggest by referee #2, some considerations have been added in paragraph 4.4 to support the local/regional argument. Our data have been compared with other urban and industrial areas. Moreover the main emission sources of $SO_2$ have been reported using the available emission inventories.

Paragraph 4.4.
Discussion part has been extended as follow:

“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 emitting $SO_2$ are represented by mineral oil and gas refineries (39.9%), manufacture of glass (32.5%), 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 has 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 concentrations detected in this study and in other areas. Compared with other European studies, the levels of sulfate are similar, but $SO_2$ concentrations are generally lower than those observed in other regions.
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 correlations ($r< 0.5$) were observed 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 $PM_{10}$)<br>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)<br>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

## *Conclusions*

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

This question has been better specified in the introduction paragraph and in paragraph 4.3.

Introduction:
"In this study an approach to easily interpret aerosol formation processes and acidity properties is proposed, 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 ratio and $NO_3^-$ concentration 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."

Paragraph 4.3
"The aforementioned articles reported an increase of nitrate concentration for $[NH_4^+]/[SO_4^{2-}]>1.5$, but this ratio is referred to different environmental conditions compared to our sampling conditions. In this study an easy method is proposed to investigate the sulfate-nitrate-ammonium system and the subsequent SIA generation processes, identifying the $[NH_4^+]/[SO_4^{2-}]$ ratio related to the sampling conditions. A *q*-mode cluster analysis using the Ward's Hierarchical agglomerative clustering method and the squared Euclidean distance measure was applied on $NO_3^-$ and $[NH_4^+]/[SO_4^{2-}]$ ratios to highlight the $[NH_4^+]/[SO_4^{2-}]$ limit ratio."

*[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.]*
We agree.

*[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.]*

Paragraph 4.3.
As described above, the relevance of the approach has been better specified.

Paragraph 4.4

*[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?]*

The cluster analysis was made on sampling days as described in Squizzato et al. (2012). This analysis was used to select groups of samples on the basis of their similar ionic composition, gaseous pollutant concentration, SOR, NOR and environmental conditions.

After the analysis, wind roses were plotted and interpreted for the days of each group. Therefore, it is possible that the days in a cluster have different wind regimes.

*[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.]*

The two clustering approaches do not have the same purpose. As reported above, in the introduction paragraph we better specified the purpose of each step of the work.

*As partially stated above, Tables 3 and 4 can be made into a figure combined with Figure 4.*

Table 3 cannot be combined with figure 4 because it is linked to the first cluster analysis.

Concerning table 4, we think that including the table in the figure can render its consultation more difficult.