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Supplement of

Chemical characteristics of size-resolved atmospheric aerosols in Iasi, north-eastern Romania: nitrogen-containing inorganic compounds control aerosol chemistry in the area

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Table S 1: Detailed statistics for the PM_{10} and $PM_{2.5}$ fractions mass concentrations determined over the investigated period (n = 84 sampling events) in Iasi, north-eastern Romania.

Applied test	$PM_{2.5}$		PM_{10}	
	p-value	Confidence level (%)	p-value	Confidence level (%)
Shapiro-Wilk normality test	0.546	95	0.682	95
t-test	0.987	95	0.998	95

Section S 1

Possible explanations for the differences/similarities between afore mentioned studies might be seen as a result of the contributions brought from various factors. As shown below the differences in the PM mass concentrations reported in Galon et al. and those reported in Arsene et al. (2011) might be only slightly controlled by changes in the particle size cut-off and/or by the difference in sampling site altitude (25 m in Galon et al. vs. 35 m in Arsene et al. (2011)) which is too small to account for the difference in PM concentrations.

In Arsene et al. (2011) study, aerosol sampling has been undertaken by using a stacked filter unit (SFUs) consisting of a 8.0 μm pore size 47-mm diameter Isopore polycarbonate filter mounted in front of a 0.4 μm pore size 47-mm diameter Isopore filter. According to details in Arsene et al. (2011) and references included therein, the 50% cut-point diameter (D50) of the 8.0 μm pore size filter was estimated to be of the order on 1.5 ± 0.2 μm aerodynamic equivalent diameter (AED). Consequently, particles collected on the 8 μm pore size filters, with a diameter larger than 1.5 μm AED, were referring to the aerosol coarse fraction, while the particles collected on the 0.4 μm pore size filters were attributed to particles with a diameter below 1.5 μm AED. In Galon et al. work aerosols samples were collected on 25 mm in diameter ungreased aluminum filters using a cascade Dekati Low-Pressure Impactor (DLPI), operating at a flow rate of 29.85 L min^{-1}. Enhanced sampling efficiency of the DLPI unit used in Galon et al. work, with regard to fine and ultrafine particles, has been observed in comparison with the SFU unit reported by Arsene et al. (2011). Parallel DLPI and SFU sampling runs (performed within January–July 2016) showed that the DLPI unit could collect in average with ~ 6 μg m^{-3} more particles than the SFU system and this observation allowed us suggesting that most probably the operational limits of the SFU system with regard to fine and ultrafine particles could suppress to some extend the values reported by Arsene et al. (2011).

The difference observed between the PM_{10} mass concentration, i.e. 18.9 ± 9.3 μg m^{-3}, reported by Galon et al. and the PM_{total} mass concentration, i.e. 38.3 ± 25.4 μg m^{-3}, reported by Arsene et al. (2011) might actually be the result of sampling in different years with emission sources of various prevalence. Implementation of environmental quality management systems in various sectors with anthropogenic activity may account for that (e.g. attempts given by the local administrative sector in settling down soil- or road-resuspended dust especially over the warm seasons by wetting the roads, protecting areas with intense building activities, etc.).

Regarding other literature available values, in a study from 2016, Alastuey et al. (2016) report for PM_{10} concentrations in Moldova (the closest point to our sampling site), values as high as ~ 25 μg m^{-3} over summer and of ~ 25–30 μg m^{-3} over winter period, yielding an annual averaged value of ~ 27.5 μg m^{-3} which is much higher than the 18.9 μg m^{-3}

value reported in the present work, for Iasi, north-eastern Romania. However, the elevated concentrations observed at the eastern sites were attributed to regional or local sources (Alastuey et al., 2016). In Alastuey et al. (2016) the author reports only the altitude above sea level (i.e. 156 m for Moldova's location) and the sampling a.g.l. is not mentioned. It might be that in Alastuey et al. (2016) study if the Moldavian sampling location was assigned as an EMEP site than the sampling a.g.l. was settled in agreement with an EC Directive recommending an a.g.l. of ~ 4 or 8 m. It is believed that the difference observed between Galon et al. site (i.e. 18.9 ± 9.3 μg m^{-3}) in comparison with other European sites might actually reflect that sampling altitude would be an important controlling factor to the atmospheric aerosol burden at a site.

In Iasi, north-eastern Romania, mass concentrations in the 5 to 10 μg m^{-3} range, for the PM_{10} and $PM_{2.5}$ fractions were especially observed in samples collected after raining events (i.e., May, June, August, and October). Such behaviour would be expected since particles from the atmosphere might be efficiently removed by precipitation (Arsene et al., 2011). However, during events with strong natural or anthropogenic contributions the PM_{10} and $PM_{2.5}$ mass concentrations exceeded the averages observed at AMOS. For example, an event collected in April 2016, from 9th to 11th, with 34.3 μg m^{-3} in $PM_{2.5}$ and 43.9 μg m^{-3} in PM_{10}, was actually highly influenced by the long range transport phenomena of African dust and marine aerosols from the Black and Aegean/Mediterranean seas (i.e., event described in detail later in the text). For other events, the exceeding fine fraction mass concentrations are believed to be a result of more variable sources (combustion, biogenic, local mineral dust, meteorological factors, etc.).

Section S 2

Beside changes in sources contributions, changes in meteorological conditions (i.e. relative humidity (RH) and wind speed (WS)) might induce distinct behaviour in the seasonal distribution of the PM. While at the investigated site over the warm seasons RH values varied in the range of ~ 30–50% and in the cold seasons in the range of ~ 45–80% we expect that at these RH values particles have proper meteorological conditions to grow. There is suggestion that in the 0 to 98% RH range, the number median diameter (NMD) may increase two-fold (from 0.018 to 0.036 μm) with the range of geometric standard deviation (σ_g) for the particle size distributions in the 1.53–2.06 range and with the larger number median diameter (NMD) having the smaller σ_g. Moreover, the authors suggest that the smaller particles grew proportionately more than the larger one (Sinclair et al., 1974).

As presented in FIG. 3 in Galon et al. work, in the 0.0556–0.946 μm particles size range, higher $dM/dlogD_p$ values over the cold seasons toward those specific for the warm seasons might actually reflect a cumulative effect induced by the contribution of the sub-micron growth particles due to higher RH values during the cold seasons. Shifts in particles diameter distribution toward higher values are expected in this case.

The observed 1.60–2.39 μm supermicrone mode is most probably a result of a more significantly contribution brought by large particles mainly associated with dust resuspension due to higher wind speeds. Although over the warm seasons averaged wind speed showed similar value to that specific for the cold seasons, monthly standard deviation toward the mean values suggested much larger dispersion. During the warm seasons, storms and rapid wind ghosts are known as often engaging important quantities of dust carrying especially particles of larger diameter.

Table S 2: Detailed statistics of linear regression analysis for $\sum_{\text{cations}}$ and $\sum_{\text{anions}}$ determined for raw ion chromatography data in the $PM_{2.5}$ and PM_{10} fractions over the total investigated period, cold and warm seasons, in Iasi, north-eastern Romania.

	$PM_{2.5}$				PM_{10}			
	$\sum_{\text{cations}}/\sum_{\text{anions}}$ ratio	r	p-value	Confidence level (%)	$\sum_{\text{cations}}/\sum_{\text{anions}}$ ratio	r	p-value	Confidence level (%)
Total period	0.69	0.94	< 0.001	99.9	0.70	0.94	< 0.001	99.9
Cold seasons	0.67	0.98	< 0.001	99.9	0.68	0.98	< 0.001	99.9
Warm seasons	0.84	0.87	< 0.001	99.9	0.86	0.86	< 0.001	99.9

Note: r–Pearson coefficient

Section S 3

The missing HCO_3^-/CO_3^{2-} has been estimated as suggested by Arsene et al. (2007) while the rationale previously proposed by Arsene et al. (2011) has been used to estimate the missing NH_4^+. Within the NH_4^+(total) fraction (defined as the sum between that derived from raw IC data and the part estimated by using the rationale of Arsene et al. (2011)), the correction for the missing NH_4^+ accounted for about 21.65 ± 25.70 % for the warm seasons while for the cold seasons the correction accounted for about 46.05 ± 18.43 %. However, when estimated missing NH_4^+ has been taken into account a significant improvement in the overall ionic balance ($\sum_{\text{cations}}$ vs. $\sum_{\text{anions})}$ was observed for both the $PM_{2.5}$ and the PM_{10} fractions (detailed statistics in Table S 3).

Section S 4

During sampling, perturbations in the gas to particle equilibrium may occur with evaporation of semi-volatile NH_4NO_3 and NH_4Cl salts from the fine particles collected on the front filters and fluctuations during sampling in temperature, relative humidity and/or pressure drop across the filters might highly affect the measurements of these species especially in urban environments (Pathak and Chan, 2005; Ianniello et al., 2011). Moreover, the total concentration of ammonium salts in $PM_{2.5}$ is usually described as a sum of the measurements both for non-volatile (unevolved) and volatile (evolved) fine particulate species (Ianniello et al., 2011). Since in the present work during sampling neither denuders nor backup-filters were used, sampling artefacts of semi-volatile NH_4NO_3 and NH_4Cl species are not completely excluded. Although presented data are reliable from the instrumental analysis point of view, limitations related to potential unmeasured species especially due to sampling procedure (during and after) should always be taken into account (i.e. potential NH_4^+, NO_3^- and Cl^- evolving from the filters as a result of NH_4NO_3 and NH_4Cl dissociations).

In Galon-Negru et al. manuscript the completeness degree of the ionic balance for the identified and quantified species in both the PM_{10} and $PM_{2.5}$ fractions was checked and quite often slopes lower than unity in the $\sum_{\text{cations}}$ vs. $\sum_{\text{anions}}$ dependences were observed in both cases indicating important cation deficit in the ionic balance. As mentioned in the manuscript, per sampled events either cation or anion deficit has been observed in various stages. For similar behavior in Arsene et al. (2011) a detailed rationale has been proposed in order to explain/estimate either missing anions or cations within the ionic budget (under subsections 3.3 Role of inter-particle and gas-particle interactions in establishing fine and coarse fractions chemical composition and 3.4 The ionic balance in the coarse and fine fractions of Arsene et al. (2011) paper). As given in Arsene et al. (2011), meteorological conditions favourable to generate deliquesced particles in the form of $NH_4NO_{3(aq)}$ and $NH_4Cl_{(aq)}$ may exist in Iasi, north-eastern Romania, with deliquesced particles being formed under conditions of relative humidity at deliquescence (RHD), a parameter which is defined as the relative humidity at which deliquescence is completed.

While in Arsene et al. (2011) high RH values were representative for the warm seasons it seems that in Galon-Negru et al. manuscript high RH values, and hence representative conditions for deliquescence to occur, were mainly prevailing during the cold seasons. As suggested in Arsene et al. (2011) under deliquescence conditions, deliquesced particles may lead to the formation of aqueous droplets by a process favouring formation of internal mixture from externally mixed particles, which actually results in changes in the activities of semi-volatile species. According to Pathak and Chan (2005) in mixed collected particles the gas-particle equilibrium will tend to re-establish by mass exchange between the gas and particulate phases. Moreover, if deliquesced particles are formed under favourable meteorological conditions, then the following reactions can occur during inter-particle or gas-particle interactions:

$$NH_4Cl_{(s)} \xleftrightarrow{RH>RHD} NH_4Cl_{(aq)} \leftrightarrow NH_4^+{}_{(aq)} + Cl^-{}_{(aq)} \leftrightarrow NH_{3(g)} + HCl_{(g)} \qquad \text{(RS1)}$$

$$NH_4NO_{3(s)} \xleftrightarrow{RH>RHD} NH_4NO_{3(aq)} \leftrightarrow NH_4^+{}_{(aq)} + NO_3^-{}_{(aq)} \leftrightarrow NH_{3(g)} + HNO_{3(g)} \qquad \text{(RS2)}$$

$$H^+{}_{(aq)} + Cl^-{}_{(aq)} \leftrightarrow HCl_{(g)} \qquad \text{(RS3)}$$

$$H^+{}_{(aq)} + NO_3^-{}_{(aq)} \leftrightarrow HNO_{3(g)} \qquad \text{(RS4)}$$

$$H^+{}_{(aq)} + NH_{3(g)} \leftrightarrow NH_4^+{}_{(aq)} \qquad \text{(RS5)}$$

with (RS1), (RS2), (RS5) being responsible for artefacting ammonium measured concentrations. While, actually, reactions (RS1) and (RS2) would be responsible for negative ammonium artefacts, reaction (RS5) would involve absorption of ammonia on aqueous droplets with positive artefacts. The competition between (RS1), (RS2) and (RS5) reactions will strongly depend on meteorological conditions directly related to RH, RHD and temperature but also on chemical species abundances. According to Pathak and Chan (2005) in ammonium reach environments, reaction (RS5) would be responsible on highly contributing artefacts in NH_4^+ and H^+ distribution, especially due to acidity neutralisation by the existent ammonia. In their work, Arsene et al. (2011) proposed a detailed rationale for a potential estimation of the unmeasured NH_4^+ fraction induced most probable by the reactions inducing negative artefacts and significantly occurring during sampling. In Galon-Negru et al. work this unmeasured NH_4^+ has been called “missing NH_4^+” and for its estimation Arsene et al. (2011) rationale has been used.

Table S 3: Detailed statistics of linear regression analysis for $\sum_{cations}$ and $\sum_{anions}$ determined when estimated missing NH_4^+ has been taken into account, in the $PM_{2.5}$ and PM_{10} fractions over the total investigated period, cold and warm seasons, in Iasi, north-eastern Romania.

	$PM_{2.5}$				PM_{10}			
	$\sum_{cations}/\sum_{anions}$ ratio	r	p-value	Confidence level (%)	$\sum_{cations}/\sum_{anions}$ ratio	r	p-value	Confidence level (%)
Total period	0.95	0.98	< 0.001	99.9	0.95	0.98	< 0.001	99.9
Cold seasons	0.97	0.99	< 0.001	99.9	0.98	0.99	< 0.001	99.9
Warm seasons	0.87	0.96	< 0.001	99.9	0.86	0.96	< 0.001	99.9

Note: r–Pearson coefficient

Section S 5

Additional information about ISORROPIA-II runs performed in the present work

The model helps deriving (even under constrains) either information related to potential H+ concentration in the aerosol particles (implicitly also on aerosols pH) or to the liquid water content (if a liquid phase exists), and computed concentrations of gas–phase semi-volatile compounds in equilibrium with the aerosol (e.g., NH_3, HNO_3, and HCl) (Hennigan et al., 2015). Although use of ISORROPIA-II model runs in forward mode with only aerosol-phase input is highly susceptible for debate, Guo et al. (2015) report also about use of the model under these specific conditions. It seems that under these circumstances the model is less sensitive to measurement error than the reverse mode. However, in Guo's et al. (2015) work, pHs reported for SCAPE were corrected for the identified bias and the values were increased by 1 to simplify the correction. Although there is suggestion that in thermodynamic model calculation (a region where the thermodynamic predictions, and assumption of equilibrium, become more accurate) only data with RH exceeding 60 % might be considered (Moya et al., 2002), in the present work ISORROPIA-II was applied over the entire set of data-base regardless RH values (in 2016, at the investigated site, July, August and September were the months with RH < 40 %). However, the model was also run at additional 5 to 10 % RH (to that experimentally recorded) in order to check RH potential influence on the envisaged estimations. It has been observed that a change in the RH value with 5 or 10 % would result actually in a pH change with about 2 and, respectively, 3 %. Since in the present work, organic species have been taken into account in the ionic balance it is believed that the bias in the estimated species (especially NH_4^+ and HCO_3^-/CO_3^{2-}) is minimized and implicitly that in inferred H^+ by ISORROPIA-II thermodynamic model.

For the present data-base, ISORROPIA-II model was run in "forward mode" for metastable aerosol. Runs were performed both for NH_4^+ derived from raw IC data and also for the situation when missing ionic species have been indirectly estimated and taken into account (NH_4^+(total) and HCO_3^-/CO_3^{2-} estimated as previously presented). For Iasi, north-eastern Romania, when ISORROPIA-II estimated H^+ has been taken into account the improvement in the overall ionic balance (in comparison with that derived by considering the NH_4^+(total) fraction) was almost insignificant with an ~ 2 % increase on the $\sum_{cations}$ vs. $\sum_{anions}$ ratio, observed in both the $PM_{2.5}$ and PM_{10} fractions. However, over the warm seasons it seems that neither NH_4^+(total) fraction option nor the one taking into account ISORROPIA-II estimated H^+ concentrations do not lead to a close to 1 ionic balance, with ratios varying between 0.84 and 0.88 for the $PM_{2.5}$ fraction and 0.84 to 0.87 for the PM_{10} fraction. Such observation would not suggest high uncertainty in the accuracy of the ionic species measured values but most probably that some volatile cation species (e.g., amines) were not measured.

Section S 6

Actually, for about 19 % of the data the aerosol pH differed by less than 1.0 pH unit when NH_4^+(total) concentrations (defined as the sum between that derived from raw IC data and the part estimated by using the rationale of Arsene et al. (2011)) increased in comparison with NH_4^+ derived from raw IC data (a (35.65 ± 24.92) % increase in NH_4^+ concentration for the entire data-base, a (21.65 ± 25.7) % increase for the warm seasons and a (46.05 ± 18.43)% (mean ± stdev) increase for the cold seasons). Such change in NH_4^+ concentrations is not unexpected since this is assigned as a highly volatile compound, with high susceptibility to be lost by evaporation. As shown in the text, meteorological parameters (i.e., RH) could play an important role within NH_4^+ distribution in both during the warm and the cold seasons. In other studies, higher evaporation rates are reported for summer when compared to winter, but during winter low RH values were prevailing (Ianniello et al., 2011; Zhao et al., 2016). Ianniello et al. (2011) report for example that in Beijing, China, about 35 % of fine particulate NH_4^+ was susceptible to evaporate from the sampling filters during winter while about 53 % of fine particulate NH_4^+ was susceptible to evaporate during summer. For the same location, Zhao et al. (2016) report NH_4^+ loss of 6 % and higher losses of NO_3^- and Cl^-.

Section S 7

In the Introduction section of Galon-Negru et al. work it has been already stated that “Particles acidity might influence transition metals solubility and enhance aerosols toxicity and atmospheric nutrient delivered through atmospheric deposition in marine areas (Meskhidze et al., 2003; Fang et al., 2017).”. Particles pH is known to affect the solubility of trace metals (such as Fe) found in aerosols (Meskhidze et al., 2003; Fang et al., 2017), with lower pH dissolving metal oxides and converting them to soluble metal sulfates (Oakes et al., 2012), conditions which would significantly change the aerosol environmental impacts. As presented in Guo et al., (2016), while at global level metal mobility will mainly affect nutrient distributions with important impacts on productivity, carbon sequestration, and oxygen levels in the ocean, at regional scales soluble transition metals seem mainly to enhance aerosol toxicity or their oxidative potential. Through SO_4^{2-} contributions to aerosols acidity and the historical record of associations between so-called particle “strong acidity” and adverse health effects, Fang et al. (2017) suggest that SO_4^{2-} linkages to health are most probably determined by SO_4^{2-} role in acid dissolution of primary metals commonly found in ambient particles, while Tsagkogeorgas et al. (2017) suggest that on a regional to global scale the acidification of fresh water and forest ecosystems is most probable caused by wet and dry deposition of SO_2 and SO_4^{2-} particles.

Epidemiological studies have often reported adverse health outcomes associated with strong aerosols acidity (Dockery et al., 1996; Gwynn et al., 2000; Lelieveld et al., 2015). In “Measuring aerosol damage to the atmosphere” (http://ec.europa.eu/research/infocentre/article_en.cfm?artid=31296, 28 October 2013), “Arsene says the high aerosol levels are probably linked to the high rate of various pulmonary diseases registered at the Clinic of Pulmonary Diseases in Iasi. These include cases like chronic obstructive pulmonary diseases (COPD), pneumonia, asthma (allergy, rhinitis), bronchiectasis (sometimes associated with bacterial infection) and tuberculosis often detected in the area.”. The claim is not a result of a systematic work on an epidemiological study in Iasi, north-eastern Romania, but it represents a general observation of Arsene after performing research work with specialists and medical doctors in the field of pulmonary diseases (Cernat et al., 2011).

Moreover, upon our knowledge there is a single report, mentioned by Arsene et al. (2007), referring to indirect evidences of acid rain impacts in Iasi region, north-eastern Romania. In the performed study, Arsene et al. (2007) calculated high wet deposition fluxes for ions of anthropogenic origin in the $SO_4^{2-} > NO_3^{-} > NH_4^{+}$ order. The determined values, although among the highest, were in generally in good agreement with values reported for other north European sites (such as those for Poland, the Czech Republic, etc.). In the analysed raining events, air masses crossing very large continental areas (N and E sectors) brought the highest contribution in terms of fluxes for ionic species such as Ca^{2+} while the NW and W sectors brought more significant contributions for anthropogenic related elements (SO_4^{2-}, NO_3^{-}, NH_4^{+}). Arsene et al. (2007) suggested that in the rainwater, higher fluxes of these elements for the NW and W sectors, when compared with other geographical sectors, was most probably also a result of important local influences, as the sampling site was located east side of the Oriental Carpathians chain that could constrain, to some extent, the pollution plume transported from western Europe. Arsene et al. (2007) report that the pH of the analysed rainwater events was 5.92 (volume weighted mean average, VWM) suggesting a sufficient load of alkaline components neutralizing rainwater acidity. Moreover, the authors suggested that on average, 97 % of the acidity in the collected rainwater samples was mostly neutralized by $CaCO_3$ and NH_3.

Section S 8

Regarding meteorological parameters, i.e. RH and temperature, in Galon-Negru et al. work is shown that over the cold season’s high RH values and low temperatures were prevailing while over the warm seasons these parameters showed opposite trends. In the work of Ianniello et al. (2011), related to chemical characteristics of inorganic ammonium salts in $PM_{2.5}$ in the atmosphere of Beijing (China), the relationship between partitions of specific nitrogen-containing inorganic species towards various parameters has been investigated. The prevailing conditions over the two investigated time-periods, i.e. 23 January – 14 February 2007 and from 2 to 34 August 2007, showed higher RH values over the summer (high temperatures) and lower RH values over the winter (low temperatures).

Ianniello et al. (2011) treats in a very complex manner the relationship existent between particulate species such as SO_4^{2-}, NO_3^{-}, Cl^{-} and NH_4^{+}, and possible partition routes in the NH_3/NH_4^{+} system. Gas-to-particle conversion (photochemical processing) or heterogeneous processes are assigned as important sources contributing to particulate NO_3^{-} abundances in the atmosphere. The authors claim that while NO_2 conversion to NO_3^{-} through photochemical processing during the winter season is expected to contribute to NO_3^{-} abundance over this period of the year, the heterogeneous formation (through condensation or absorption of NO_2 in moist aerosols) generally relates to relative humidity and the particulate atmospheric loading (Ianniello et al., 2011). The existence of large amounts of particulate NO_3^{-}, observed in summer by Ianniello et al., 2011, was considered as unexpected since NH_4NO_3 is semi-volatile and tends to dissociate and remain in the gas phase under high temperatures. Ianniello et al., (2010) report 6 times higher NH_3 concentrations in summer than in winter, with temperatures ranging from 1 to 14 °C in winter and 22 to 35 °C in summer periods. Under these circumstances high concentrations of fine particulate NO_3^{-} in summer period were attributed to the existence of higher concentrations of NH_3 in the atmosphere, available to neutralise not only H_2SO_4 but also HNO_3 from the atmosphere. In addition, at the high RH values (daily mean in the 35 to 90 % range) reported in Ianniello et al. (2011) study significant fraction of HNO_3 and NH_3 were considered to be dissolved in humid particles, with enhanced distribution of fine particulate NO_3^{-} and NH_4^{+} in the atmosphere.

In Galon-Negru et al. work particulate NH_4^{+} showed higher values during the cold seasons when compared to the warm seasons and its variation coincide with those of fine particulate NO_3^{-} and Cl^{-}. Although such behaviour would indicate that NH_4^{+} was largely originating from the neutralization between ammonia and acidic species such as HNO_3 and HCl, as shown under Subsection 3.2.3 (Stoichiometry of $(NH_4)_2SO_4$, NH_4NO_3 and NH_4Cl), the most important contribution was most probably brought by H_2SO_4 species. However, the very similar pattern observed for NO_3^{-}, Cl^{-} and NH_4^{+} suggest that these species were representative for likely internally mixed particles and came most probably from similar gas-to-particle processes (Huang et al., 2010). Galon et al. report for SO_4^{2-} comparable concentrations during both the summer and winter seasons, and Backes et al. (2016a) suggest that the formation of SO_4^{2-} particles is not limited by NH_3 in any season. During the warm seasons, higher temperatures and solar radiation intensity, enhancing the photochemical activity and the atmospheric oxidation potential, is also enhancing the oxidation rate of SO_2 to particulate SO_4^{2-}, but during the cold seasons wood burning might become an important source of SO_4^{2-}.

At high RH values, and especially for deliquescent particles, there is suggestion that most of the fine particulate NO_3^{-} exists as an internal mixture with SO_4^{2-}, so that HNO_3 can be easily absorbed into the droplets, a process considerably reducing the thermodynamic dissociation constant for NH_4NO_3 (Zhang et al., 2000; Ianniello et al., 2011). Under these circumstances it is supposed that fine particulate NO_3^{-} can be formed from HNO_3 and NH_3 through heterogeneous reactions on fully neutralised fine particulate SO_4^{2-} (a process which has been taken into account also in Galon et al. work, under the Subsection 3.2.3). In Galon et al. work significant correlation has been observed between SO_4^{2-} and NO_3^{-}. These two measured parameters showed significant correlation with the RH, with high concentrations in SO_4^{2-} or NO_3^{-} being formed at high RH values. Such behaviour would allow us suggesting that NO_3^{-} is being produced on preexisting SO_4^{2-} aerosols, which could provide sufficient area and aerosol water content for the heterogeneous reaction to occur should be available.

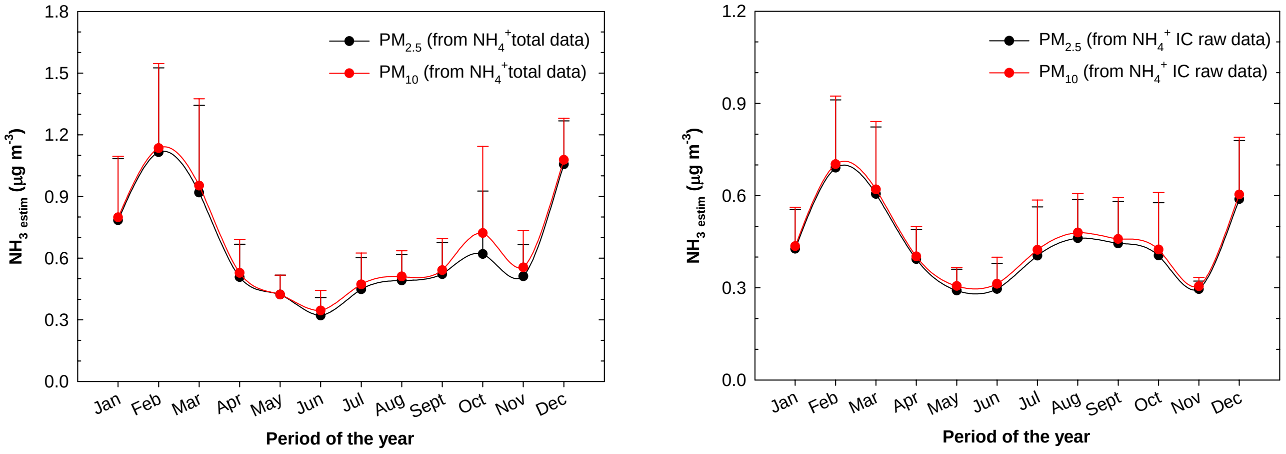
Markovic et al. (2011) show that at high RH, the amount of the gaseous precursors, such as NH_3 and HNO_3, have relatively little influence on the formation of fine particulate nitrate. Ianniello et al. (2011) concluded also that in summer period, with high prevailing RH values, almost on all days the meteorological conditions were favourable for the formation of NH_4NO_3 at Beijing site.

In Galon et al. work, regarding gaseous NH_3 values such as those derived from ISORROPIA, it should be pointed out that its estimated concentration was much higher than that of HNO_3 and HCl in gas phase. During the cold seasons the $[NH_3]/([HNO_3] + [HCl])$ ratio is as high as 2.0 ± 0.6 for RH values < 40 %, 3.6 ± 2.0 for RH values in the 40–60 % range, and 3.0 ± 1.4 for RH values > 60 % RH. During the warm seasons, for similar RH groups, the ratio takes the 4.9 ± 1.9, 4.6 ± 1.4 and $9.1.0 \pm 6.2$ values. Ianniello et al. (2011) report a $[NH_3]/([HNO_3] + [HCl])$ ratio of 27.90 ± 12.70 for winter season and of 54.06 ± 20.60 for the summer period. The authors are finally claiming that the atmosphere of their interest location was ammonia-rich in gas phase over both investigated seasons.

Moreover, for the specific conditions referring to Galon et al. work, the authors have observed that by analysing the events for similar RH groups, but for cold and warm seasons separately, the NH_3/NH_4^+ partition didn't enhance significantly. During the cold seasons over the three RH investigated groups, the fractions of the NH_3, HCl and HNO_3 present in the gaseous form have taken in average the 71.4 ± 4.7, 4.4 ± 0.3 and $24.0 \pm 4.8\%$ values. Over the warm seasons for the previously mention species the fractions present in the gaseous form have taken in average the 83.1 ± 3.4, 6.6 ± 0.6 and $10.3 \pm 3.4\%$ values.

Section S 9

Backes et al. (2016a,b) present in some of their publication seasonal distributions in NH_3 emissions under static- and dynamic-time profile (STP and DTP) scenarios. While the STP scenario lacks dynamic, meteorology dependent or specific differences in policies or intensity of animal husbandry, the DTP scenario takes into account potential meteorological variables (such as wind speed and surface temperature) influence on the distribution of the annual emissions. However, while under the STP scenario, the annual time series of NH_3 showed one annual peak in spring (March), in the DTP scenario NH_3 concentrations show two annual peaks, one in spring (May) and one in autumn (September). The authors underline that implementation of the DTP resulted in a shift from seasonal average winter NH_3 emissions to summer emissions. According to Backes et al. (2016a), high NH_3 concentrations are known to appear in proximity to emission sources, due to its low atmospheric lifetime which results in NH_3 concentration levels in the atmosphere which closely follow the seasonal emission trend.



(a) (b)

Figure S 1: Time series in NH_3 concentrations derived from ISORROPIA-II runs for the 2016 data-base, both for $PM_{2.5}$ and PM_{10} scenarios in Iasi, north-eastern Romania.

Moreover, Sutton et al. (2013) claim that together with increased anthropogenic activity, global NH_3 emissions may increase from 65 (48–85) Tg N in 2008 to about 132 (89–179) Tg N by 2100. Most NH_3 emissions are known to result from agricultural productions strongly influenced by climatic interactions. There is, however, recognition about the fact that most of the up to now used approaches failed in recognising that a warm dry-year would tend to give larger NH_3 emissions than a cold-wet year. Estimates in the global NH_3 emission made by Sutton et al., (2013) indicate agricultural soils and crops, including emissions from grazing and land application of animal manure, as a first ammonia ranked source with 28.3 Tg N yr^{-1} contribution. This is immediately followed by excreta from domestic animals (8.7 Tg N yr^{-1}), oceans and volcanoes (8.6 Tg N yr^{-1}), biomass burning (5.5 Tg N yr^{-1}), waste composting and processing (4.4 Tg N yr^{-1}), and by other sources with contributions of < 3.3 Tg N yr^{-1}.

Details presented in FIG. S 1 clearly show that for Iasi, north-eastern Romania, yearly NH_3 distributions as derived from ISORROPIA-II model present clear maxima in February and December in a behaviour suggesting important local sources contributions over the winter season. It might be that this distribution follows actually a trend mainly controlled by the agricultural practices in rural areas surrounding Iasi, mainly related to the timing of manure spreading on agricultural soils. Moreover, in Iasi and in the nearby counties, the contribution brought by open (sheep and goat) barns, operating over the cold season mainly in a “hot-spot” mode, might increase as importance. Manure storage from local and regional closed barns (pigs and poultry) might also bring important contributions over the winter. Although biomass burning might bring important contribution in terms of global ammonia emissions it is believed that at the interest location this source is overwhelmed by agricultural practices in the area.

Table S 4: Detailed statistics of linear regression analysis for major water soluble ions determined in the $PM_{2.5}$ and PM_{10} fractions over the total investigated period in Iasi, north-eastern Romania.

	PM fraction	Slope	Pearson coefficient (r)	p-value	Confidence level (%)
Cl^- vs. RH	$PM_{2.5}$; PM_{10}	+	> 0.71	0.010	95.4
Cl^- vs. T	PM_{10}	-	> 0.59	0.045	95.4
Cl^- vs. PM	$PM_{2.5}$; PM_{10}	+	> 0.70	0.038	95.4
Cl^- vs. MLD	$PM_{2.5}$; PM_{10}	-	> 0.69	0.012	95.4
NO_3^- vs. RH	$PM_{2.5}$; PM_{10}	+	> 0.84	< 0.001	99.9
NO_3^- vs. T	$PM_{2.5}$; PM_{10}	-	> 0.94	< 0.001	99.9
NO_3^- vs. MLD	$PM_{2.5}$; PM_{10}	-	> 0.84	< 0.001	99.9
NO_3^- vs. PM	$PM_{2.5}$; PM_{10}	+	> 0.70	0.021	95.4
SO_4^{2-} vs. RH	$PM_{2.5}$; PM_{10}	+	> 0.44	0.177	68
SO_4^{2-} vs. T	$PM_{2.5}$; PM_{10}	-	> 0.41	0.214	68
SO_4^{2-} vs. PM	$PM_{2.5}$; PM_{10}	+	> 0.45	0.162	68
NH_4^+(total) vs. RH	$PM_{2.5}$; PM_{10}	+	> 0.80	0.001	95.4
NH_4^+(total) vs. T	$PM_{2.5}$; PM_{10}	-	> 0.94	< 0.001	99.9
NH_4^+(total) vs. MLD	$PM_{2.5}$; PM_{10}	-	> 0.80	0.001	95.4
NH_4^+(total) vs. PM	$PM_{2.5}$; PM_{10}	+	> 0.70	0.023	95.4

Note: RH–relative humidity; T–temperature; MLD–mixing layer depth; PM–particle loading;

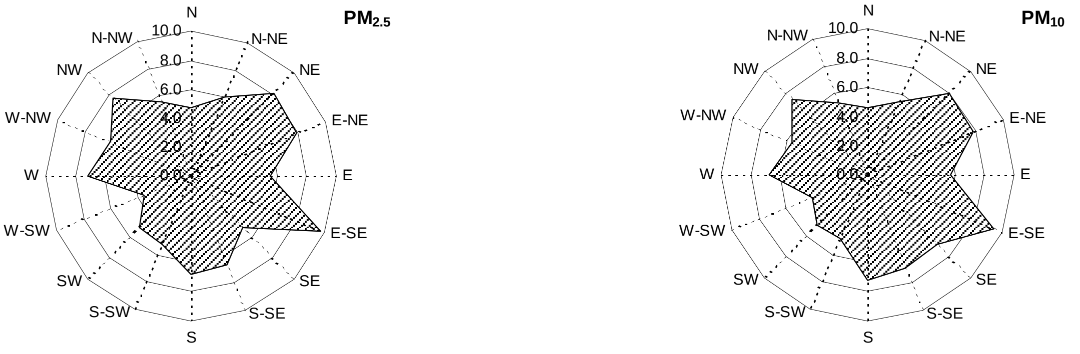
Table S 5: Detailed statistics of linear regression analysis for molar concentrations of particulate NH_4^+ and SO_4^{2-} in PM_{10} fraction over the cold and warm seasons in Iasi, north-eastern Romania.

	NH_4^+ from raw IC data			NH_4^+(total)		
	Pearson coefficient (r)	p-value	Confidence level (%)	Pearson coefficient (r)	p-value	Confidence level (%)
Cold seasons	0.97	< 0.001	99.9	0.96	< 0.001	99.9
Warm seasons	0.98	< 0.001	99.9	0.97	< 0.001	99.9

Section S 10

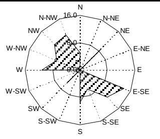
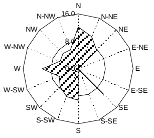
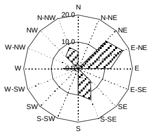
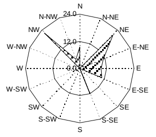
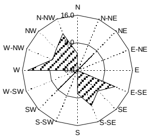
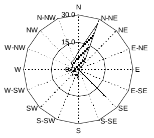
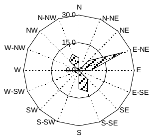
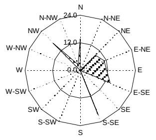
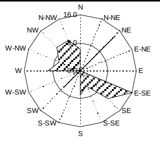
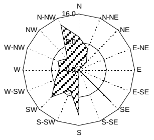
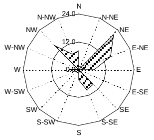
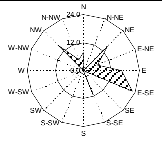
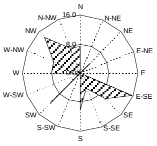
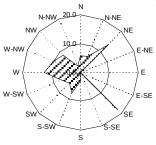
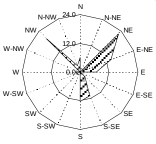
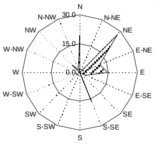
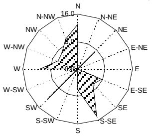
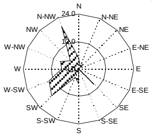
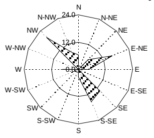
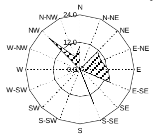
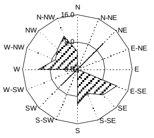
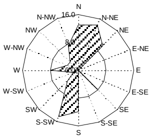
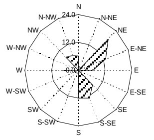
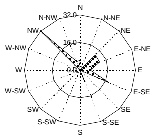
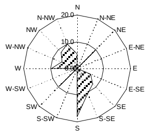
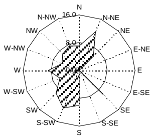
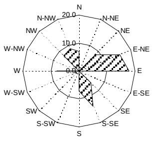
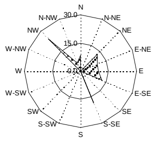
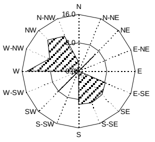
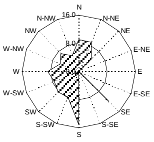
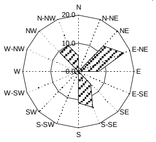
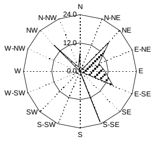
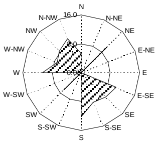
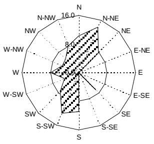
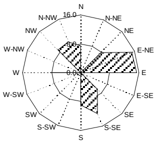
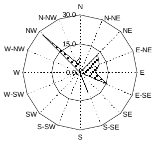
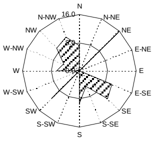
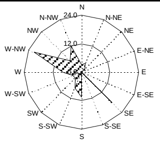
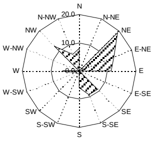
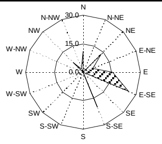
The data set from the present work has been investigated through Radar and/or Pie charts in order to identify the potential contributions brought by various sectors long-range transport to the atmospheric PM burden in the area. It should be however emphasized that the PM chemical composition appeared to be mainly driven by the air mass origin and type (e.g., continental, regional), meteorologically-controlled air mass characteristics (buoyancies), geographical context (the Oriental Carpathians chain, with the highest altitude of 1907 m, is facing Iasi ~ 150 km north-westerly distance), etc. As presented in FIG. S 2a, in overall, in terms of sectors contributions the N-NE up to the S (clockwise round) area seems to bring the most important fraction to both the $PM_{2.5}$ and PM_{10} abundances. Higher loaded events in terms of aerosols mass concentration were those associated with long-range continental transport, Saharan dust-events, regional transport from more arid areas (S-SE) and buoyancy affected air masses.

Regarding potential local anthropogenic contribution to PM atmospheric burden it should be emphasized that in the immediately nearby area of the sampling point neither important commercial areas nor industrial units are operating and traffic should be the most important contributor. Actually in Iasi, in the post-communist period, the industry has almost completely ceased down and presently the Antibiotic company (7 km from the sampling point, western, W, direction), a small brick plant (8 km, SE) and the heat and power plant (5 km, SE) may account as for the most significant local anthropogenic contributors. However, Iasi is known as an important Romanian university centre (> 42000 students by 2015) with intense activity over university semesters. Traffic in the nearby area and commercial activity in the top hot-spots area of Iasi get more intense over these periods of the year. As for the rural areas surrounding Iasi, or from the nearby counties, farming activities are mainly related to cereal crops, plantation agriculture, open and closed animal barns (cattle, sheep and goat, pigs, poultry).



(S 2a) (S 2b)

Figure S 2: Averaged annual sectors contributions both in the $PM_{2.5}$ (S 2a) and PM_{10} (S 2b) fractions.

	Winter	Spring	Summer	Autumn
$PM_{2.5}$				
Fo				
Cl^{-}				
HCO_3^{-}				
Ac				
NO_3^{-}				
SO_4^{2-}				
Ox				
NH_4^{+}				
Na^{+}				

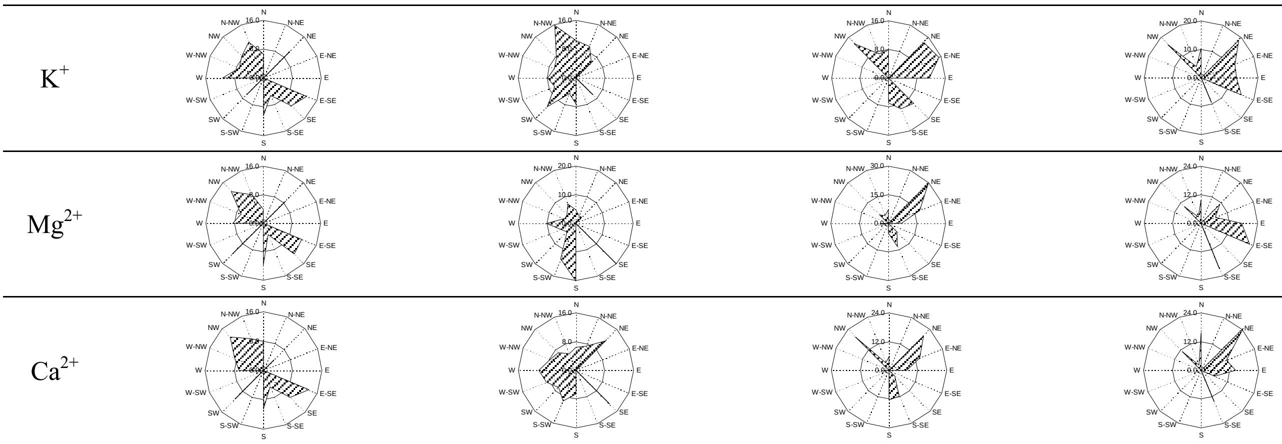
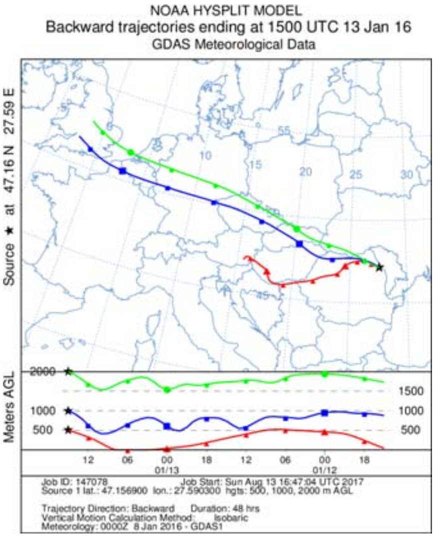
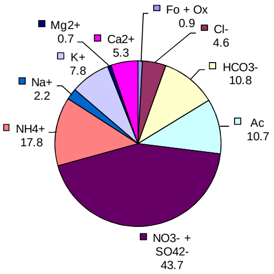


Figure S 3: Particulate inorganic and organic ions seasonal contributions (in the $PM_{2.5}$ fraction) associated with the different identified air mass.





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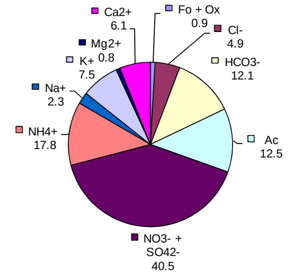

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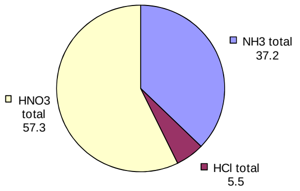

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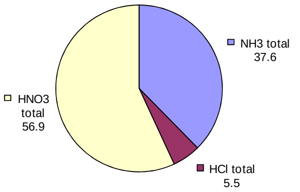

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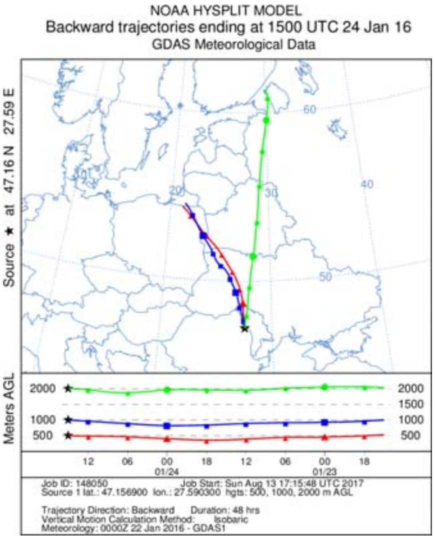

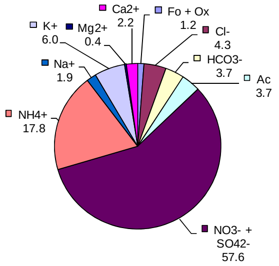

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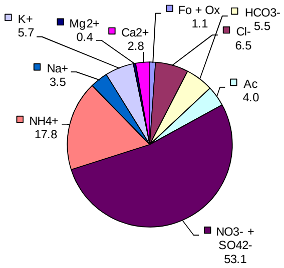

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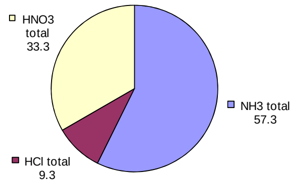

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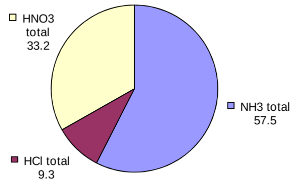

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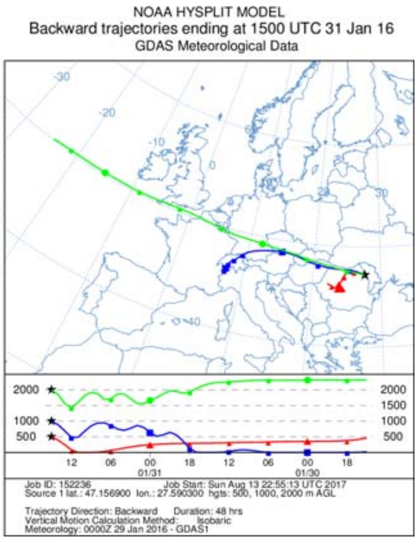

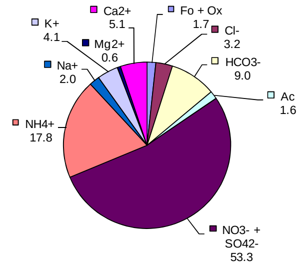

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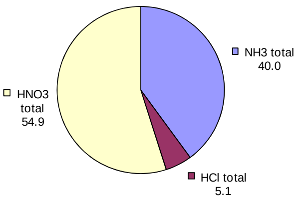

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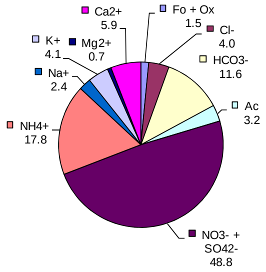

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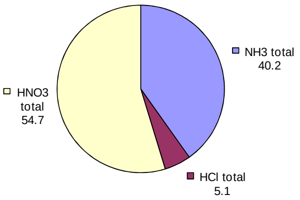

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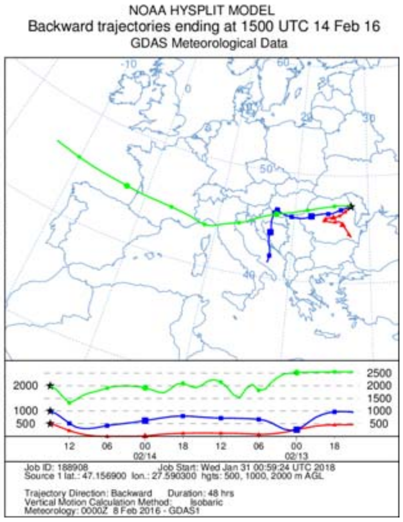

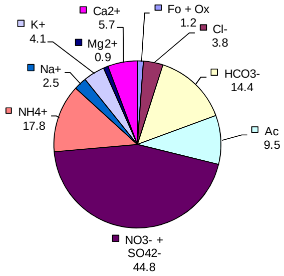

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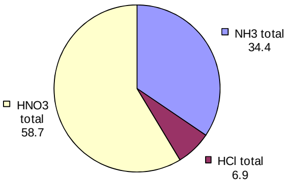

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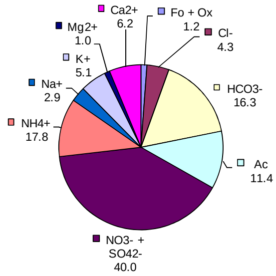

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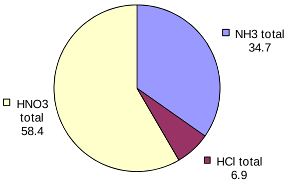

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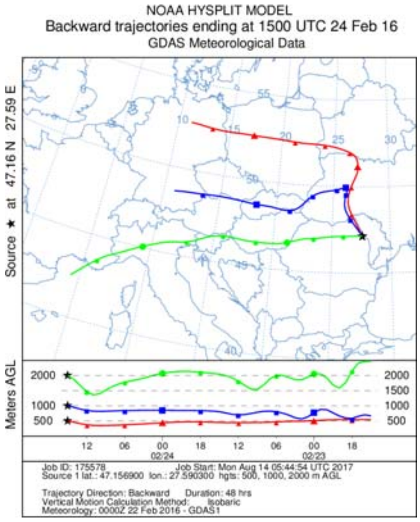

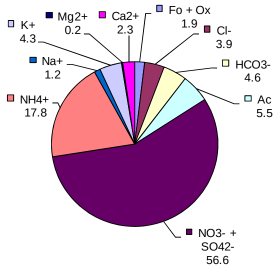

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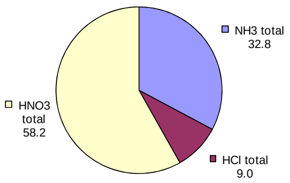

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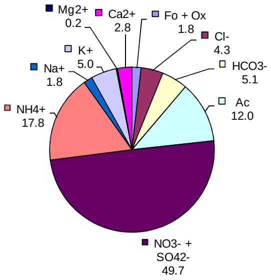

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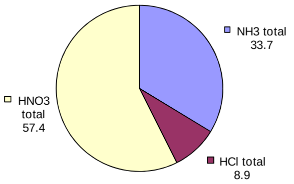

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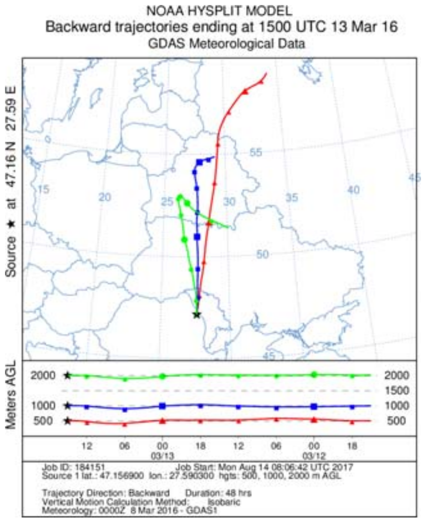

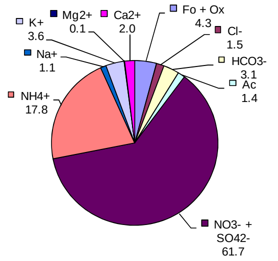

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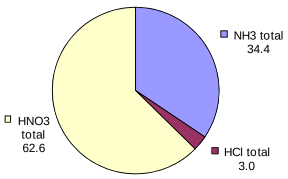

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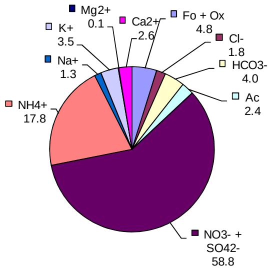

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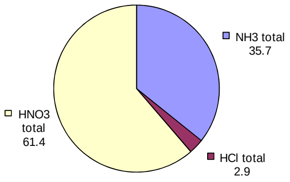

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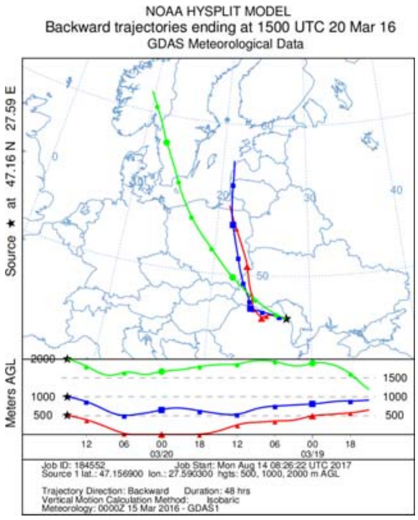

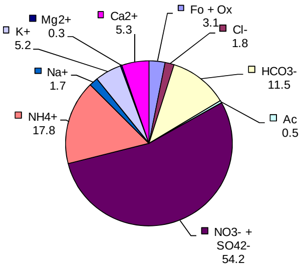

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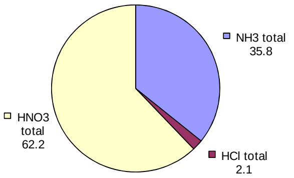

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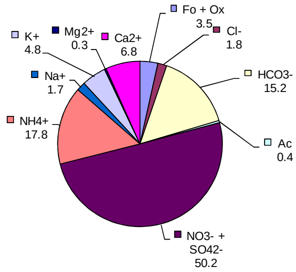

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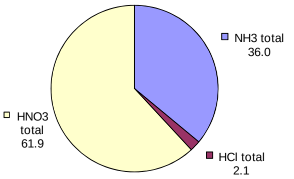

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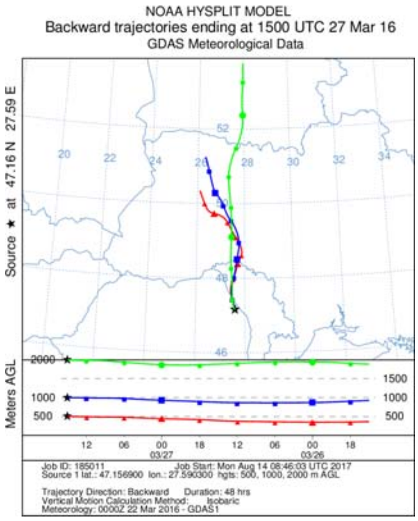

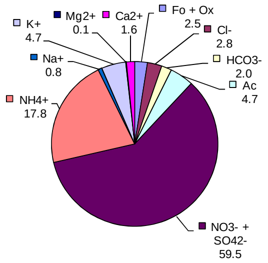

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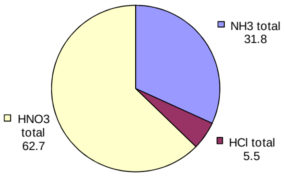

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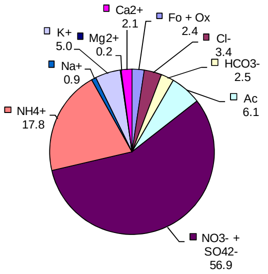

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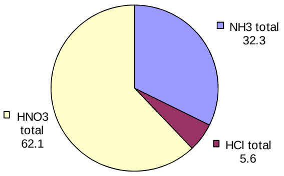

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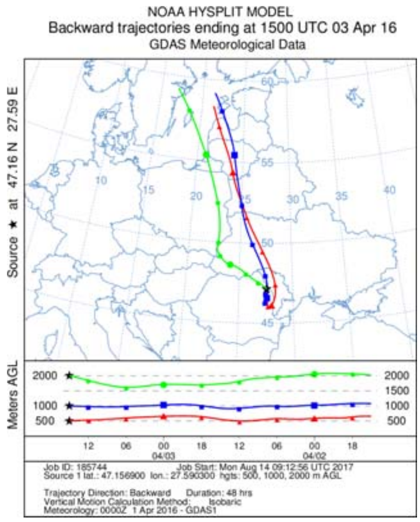

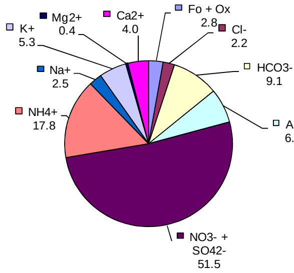

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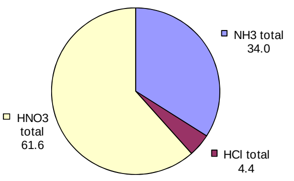

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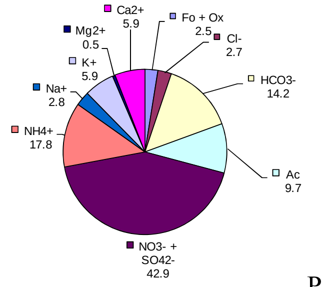

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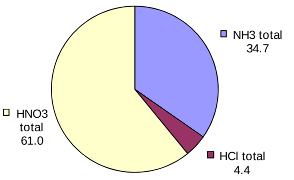

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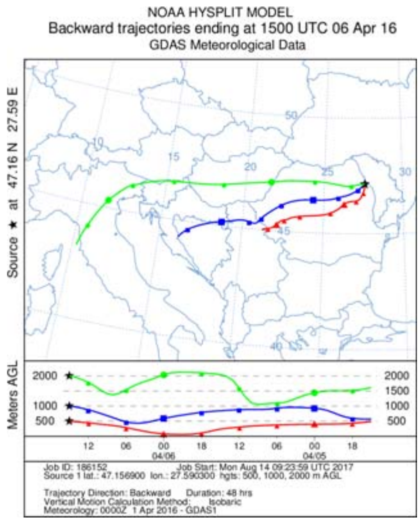

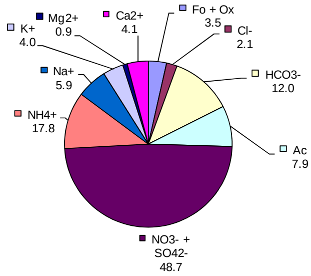

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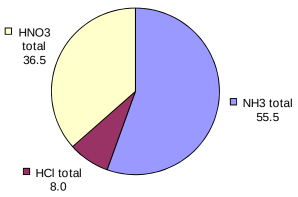

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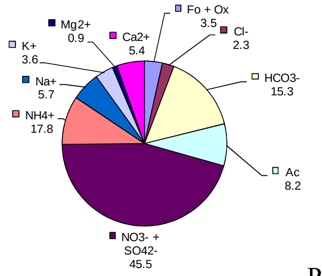

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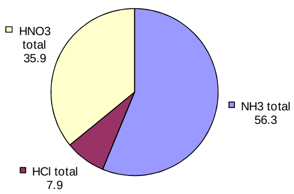

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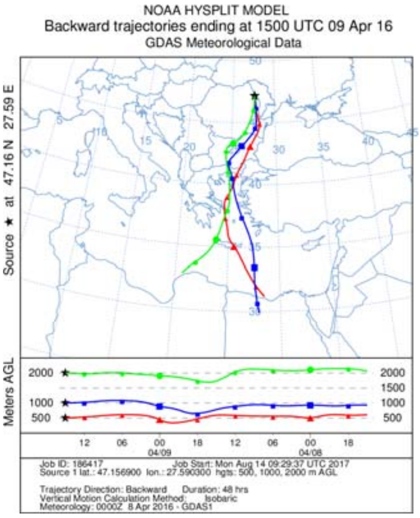

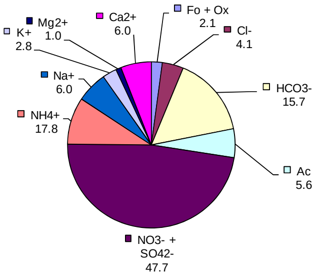

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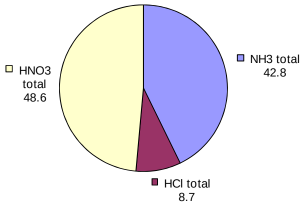

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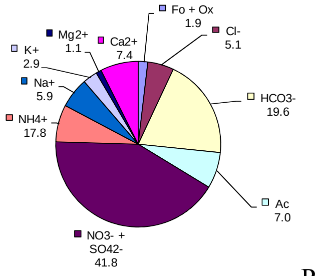

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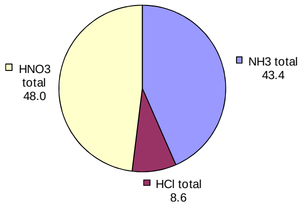

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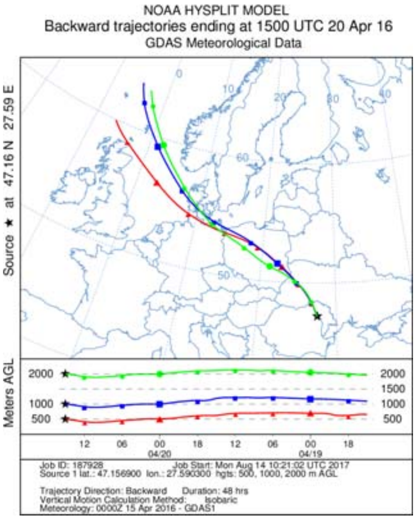

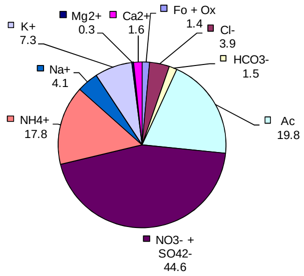

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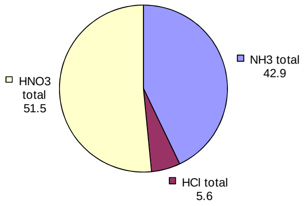

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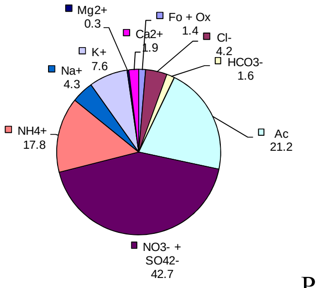

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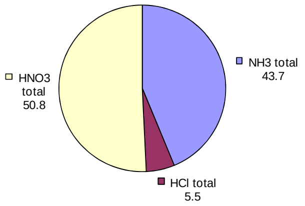

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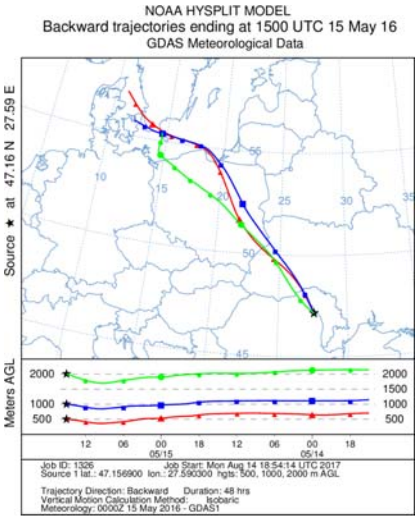

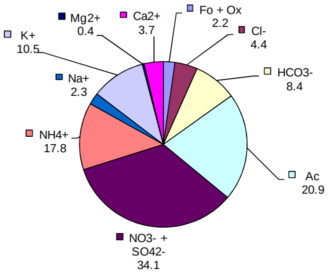

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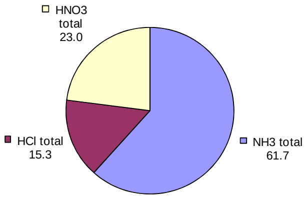

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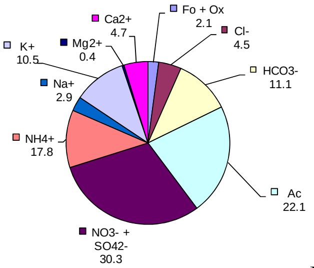

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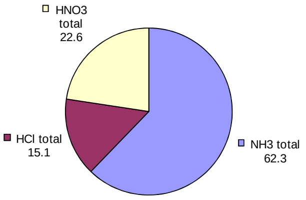

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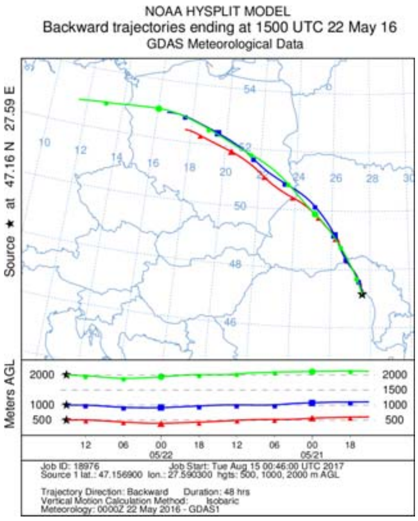

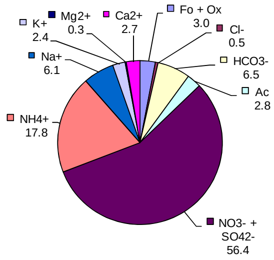

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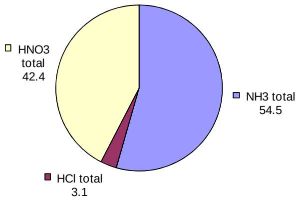

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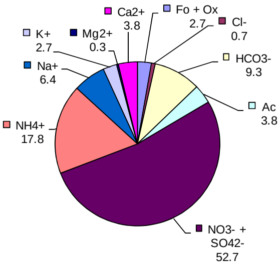

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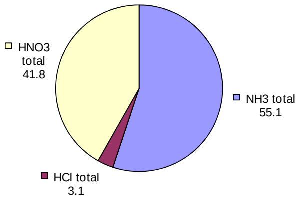

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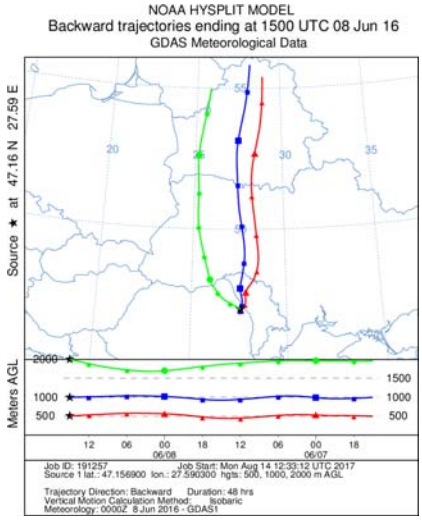

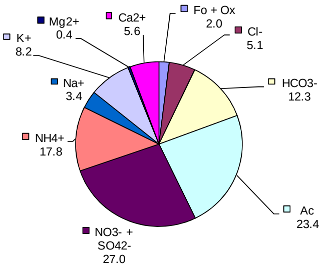

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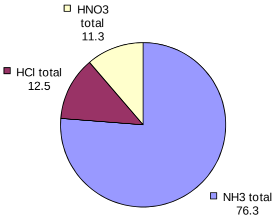

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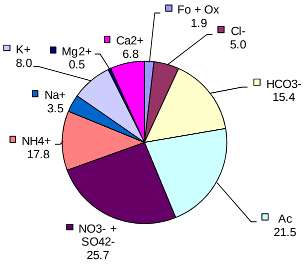

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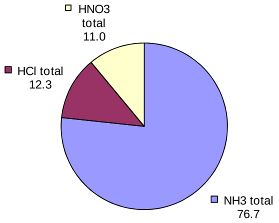

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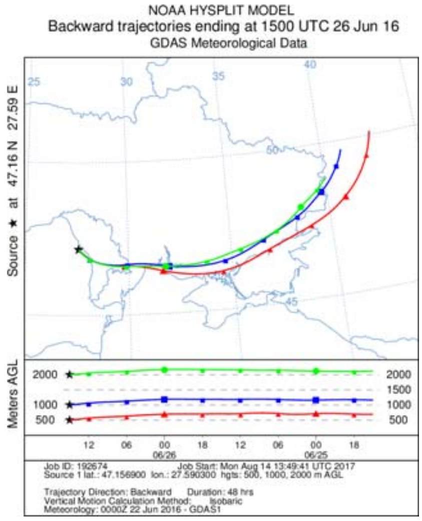

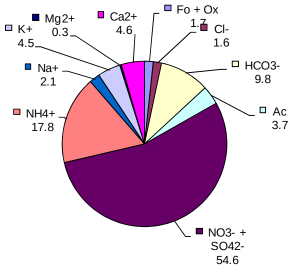

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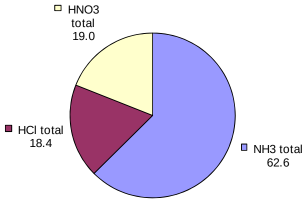

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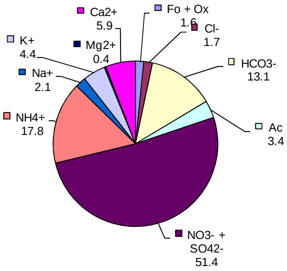

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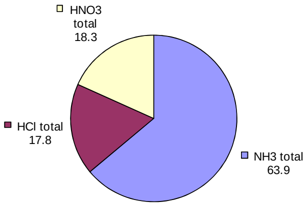

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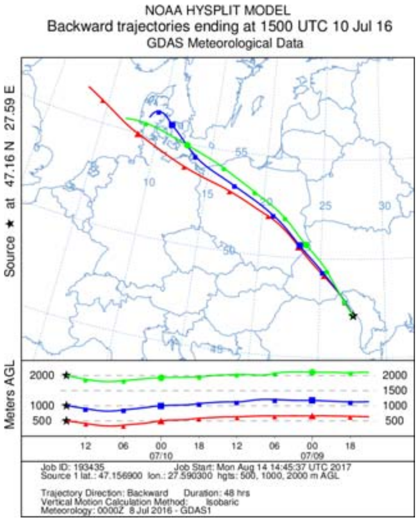

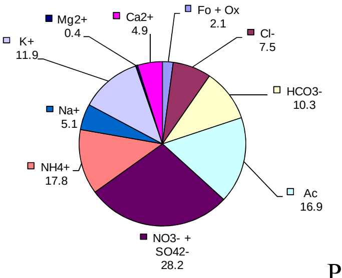

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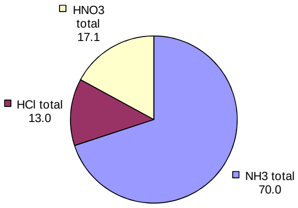

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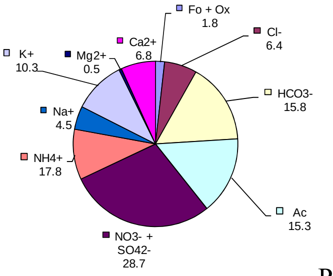

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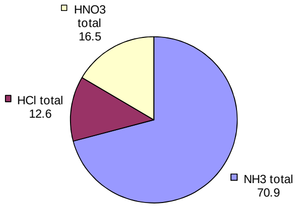

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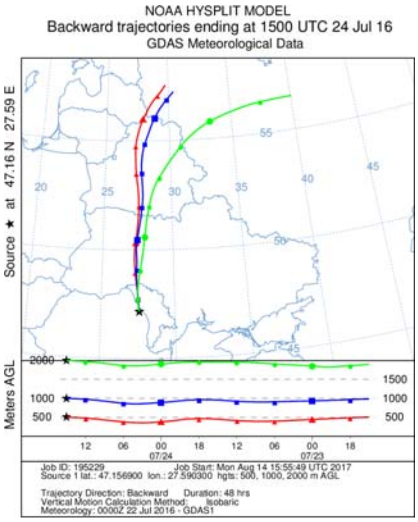

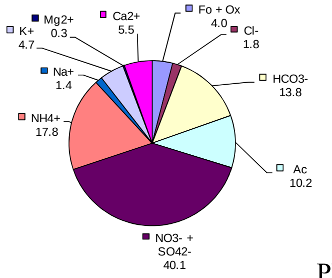

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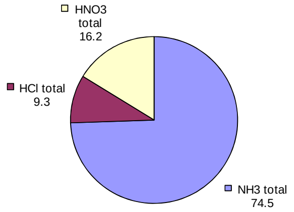

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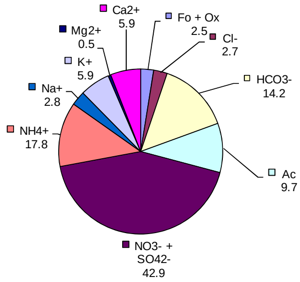

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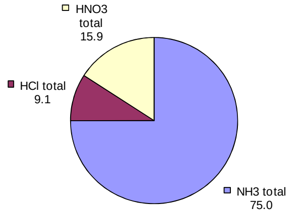

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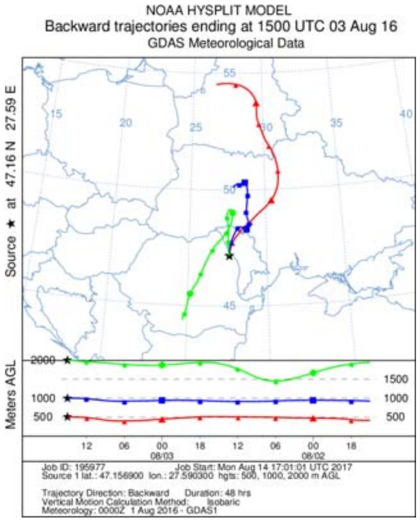

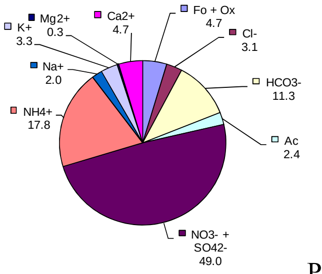

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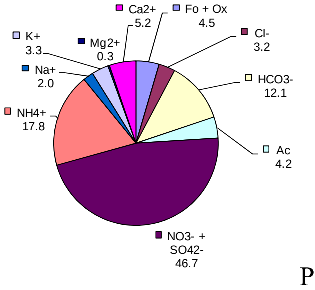

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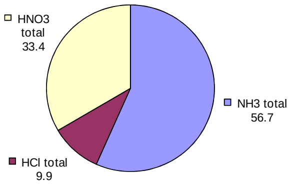

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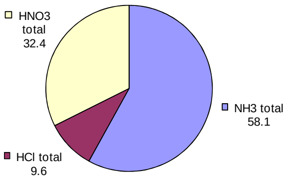

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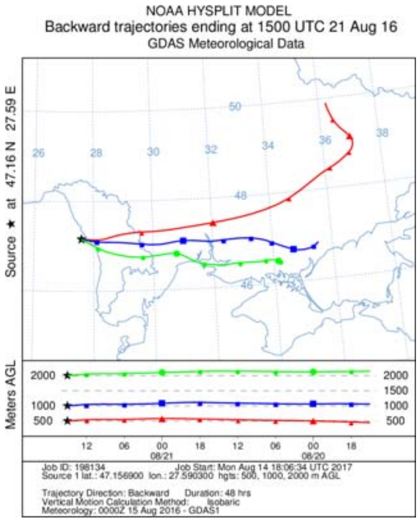

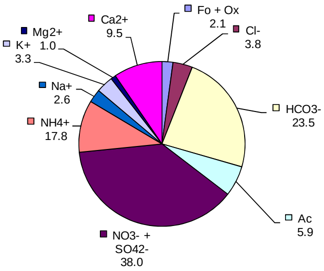

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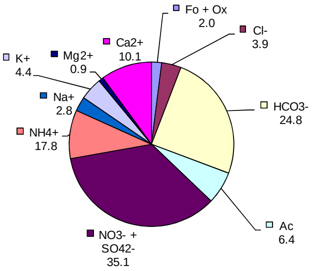

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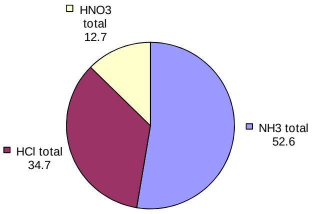

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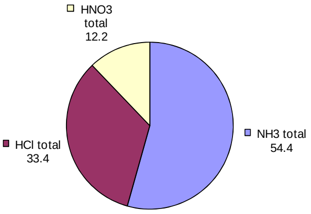

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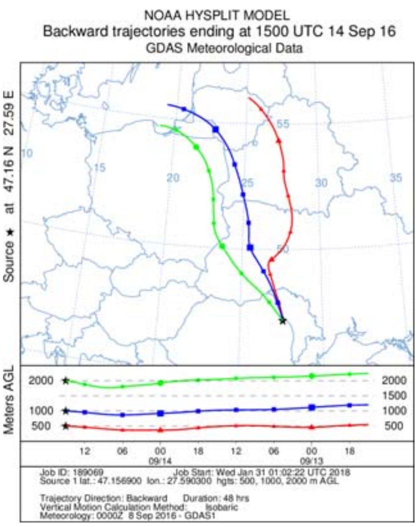

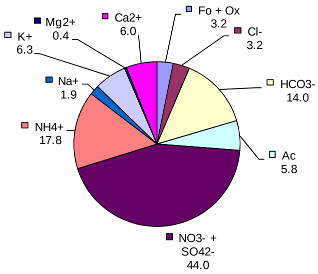

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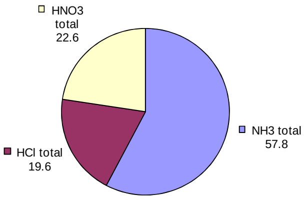

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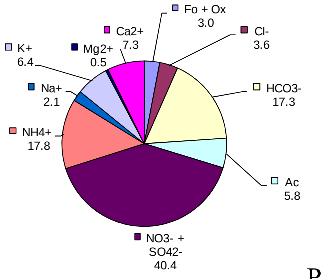

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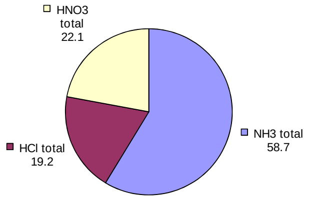

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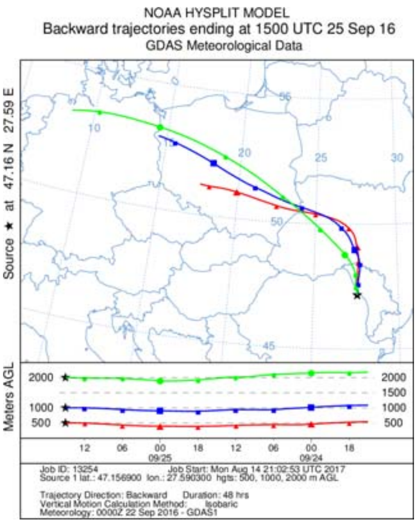

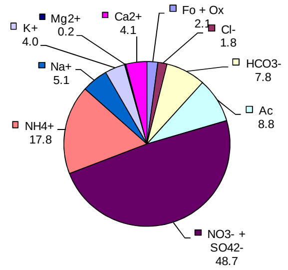

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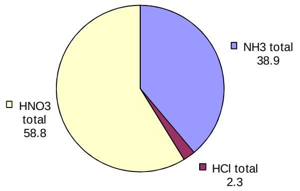

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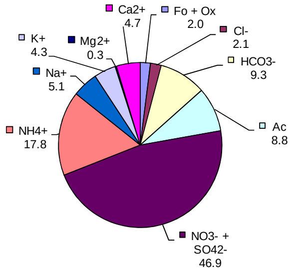

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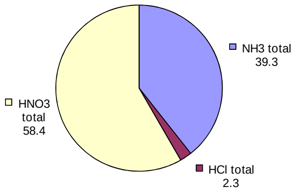

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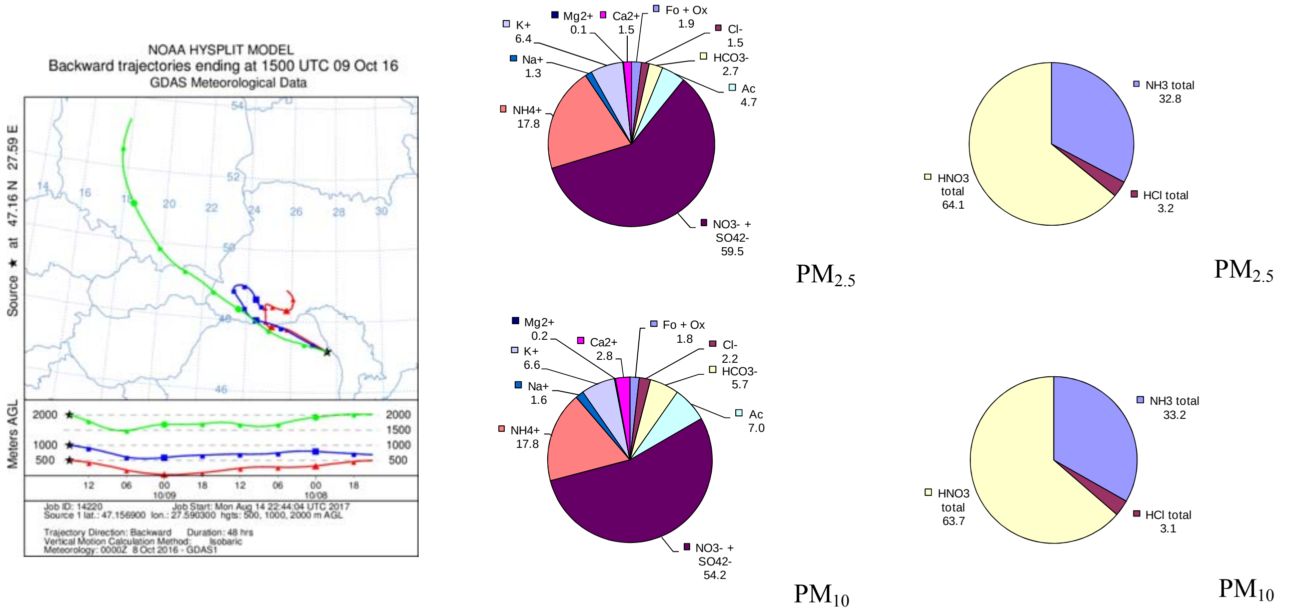

Figure S 4: Trajectory air mass associated percentual contributions for the identified-quantified ions and ISORROPIA-II predicted gaseous NH_3, HNO_3 and HCl both in $PM_{2.5}$ (top) and PM_{10} (bottom) fractions. Selected investigated events are presented. Note: Fo – formate, Ac – acetate, Ox – oxalate, NH_4^+ reflects $NH_4^+{}_{total}$.

It should be also underlined that for ionic species specific for the coarse fraction, i.e. Na^+ and Ca^{2+}, the maxima seems to be mainly induced either by the prevalent direction of the air masses (spring maxima of Na^+ ion most probably induced by the fact that March and April appeared as months with prevalent southern air masses crossing large continental areas with more salty soil) or by the drought (the summer maxima of Ca^{2+} was mainly influenced by the ionic chemical composition of aerosol samples collected in August 2016, 7 events, a month of the 2016 year without any single raining events). Actually, in August 2016, 1 event was strongly affected by atmospheric driven buoyancy (18.2 % fine particulate Ca^{2+} and 42.1 % fine particulate HCO_3^-), 1 event was affected by turbulent local air masses (10.7 % fine particulate Ca^{2+} and 24.8 % fine particulate HCO_3^-) and other 3 events showed contributions brought by air masses crossing larger continental areas (9.8 ± 1.7 % fine particulate Ca^{2+} and 25.3 ± 3.9 % fine particulate HCO_3^-). Other 2 events sampled at the beginning of August 2016 (of N-NW direction both) in terms of Ca^{2+} and HCO_3^- brought contributions as high as (4.3 ± 0.6 % fine particulate Ca^{2+} and 9.7 ± 2.3 % fine particulate HCO_3^-). High percentual contributions within the identified and quantified species brought by Ca^{2+} and HCO_3^- ions were also observed in various events collected all year round which were affected by long-range transport air masses accompanied by atmospheric driven buoyancy or by long-range transport air masses coming from arid areas (e.g. 31 January 2016, 14 February 2016, 20 March 2016, 06 April 2016, 09 April 2016, etc). It has been observed that in average the contributions brought by such events were strongly affecting the distribution of the ionic chemical composition in sampled aerosols.

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