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Chemical characteristics of atmospheric bulk deposition in a semi-rural area of the Po Valley (Italy)

Laura Tositti[1] · Linda Pieri[2] · Erika Brattich[1] (iD) ·
Silvia Parmeggiani[1] · Francesca Ventura[2]

Abstract This study provides an analysis of a five-year time series chemical composition of the bulk deposition (2009–2013), collected within a farm surrounded by industrial and urban settlements in a semi-rural area of the Po Valley, with the aim of characterizing potential emission sources affecting precipitation composition at the site. Most monitoring efforts in this region, recognized as one of the most polluted in the world both due to the intense industrialisation and urbanisation as well as to frequent air stagnation conditions, are presently devoted more to gaseous and particulate pollutants than to precipitation chemistry. The bulk deposition samples were very concentrated in chemical species, both acidic and alkaline, high compared to other polluted sites in the world and to locations in the same district. The mean ions concentrations (in $\mu eq \; l^{-1}$) are: NO_3^- (243) > SO_4^{2-} (220) > PO_4^{3-} (176) > Cl^- (153) > NO_2^- (29) > F^- (2.6); NH_4^+ (504) > Ca^{2+} (489) > K^+ (151) > Na^+ (127) > Mg^{2+} (127). pH data shows a trend toward slightly alkaline conditions attributed to the large presence of ammonium and crustal elements, in spite of high concentrations of nitrates and sulphates. The relevant concentrations of Ca^{2+} and Mg^{2+} further suggests that these alkaline conditions might be due to the correspondingly significant concentrations of carbonates/bicarbonates in our dataset. While back-trajectories analysis suggests the stronger importance of local resuspension over long-range transport, statistical analyses on ion composition highlight the key role exerted by agricultural activity, especially in the case of NH_4^+, K^+, Ca^{2+} and PO_4^{3-} (especially linked to fertilisation practices and soil resuspension due to mechanical operations). Apart from Na^+ and Cl^- ions which correlate well as expected, indicating their likely common origin from marine salt, the identification of the origin of the

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✉ Erika Brattich
    erika.brattich@unibo.it

[1]   Department of Chemistry «Giacomo Ciamician», University of Bologna, Bologna, Italy

[2]   Department of Agricultural Sciences, University of Bologna, Bologna, Italy

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other ions is very complex due to the contribution of diverse local sources, such as industrial and residential settlements.

1 Introduction

Atmospheric deposition (dry and wet) has a relevant impact on environments, affecting the nutrients cycle in agro and aquatic ecosystems, contributing to the chemical composition of plants, soils and surface waters (Pieri et al. 2010) and to the alteration of the natural resources (e.g. Fenn et al. 2003).

The chemical composition of atmospheric deposition is closely associated with aerosols which are partly dry-deposited within complex physical mechanisms, relying either on gravitational settling (mostly particles >1 μm), or on turbulence driven collision and subsequent adhesion (particles with a diameter < 1 μm). The largest fraction of ambient aerosol, however, is removed by wet deposition to which aerosol particles are closely linked, since the formation of water droplets/crystals, within the so-called nucleation, is based on the availability of ultrafine (< 100 nm) particles, promoting water condensation. As known, droplets may intercept ambient aerosol during their growth in in-cloud processes, but also during their fall to the surface (below-cloud processes). Owing to the close relationships with aerosol chemistry, inorganic ions constitute a major component of atmospheric deposition, even if trace elements, organic substances and insoluble components of both natural and anthropogenic origin may also be present (Levin and Brenguier 2009). The presence of ions affects the pH of precipitation. The pH of uncontaminated precipitation ranges between 5 and 5.6, due to the equilibrium with atmospheric CO_2 and its weakly acidic reaction in water (Vong et al. 1985; Rao et al. 1995). A lower pH value, which identifies an acid rain, is basically caused by the occurrence of further acidic species, in particular sulphuric and nitric acids derived by the oxidation of SO_2 and NO_x, while a pH value higher than 5.6 identifies an alkaline rain, generally associated with desert dust, rich in crustal elements. This is the case of regions located in the Mediterranean basin that despite high concentration of nitrates and sulphates are generally characterized by alkaline rains (Anatolaki and Tsitouridou 2009; Santos et al. 2011; Calvo et al. 2012; Durašković et al. 2012; Al-Khashman et al. 2013; Morales-Baquero et al. 2013).

As far as wet deposition is concerned, the dynamical and substantially fast processes (both physical and physico-chemical) prevent the straightforward distinction of chemicals typical of the nucleation step from those entrapped during precipitation fall. Overall, the collected deposition represents in principle both local and distant aerosol sources. In general rainout processes are related to long-range transport, while the washout component reflects a more local character (e.g., Bertrand et al. 2008).

Precipitation chemistry has been historically monitored in several networks in the world (e.g., European Monitoring and Evaluation Programme (EMEP) -www.emep.int- in Europe and the National Atmospheric Deposition Program (NADP) in USA - http://nadp.sws.uiuc.edu/NADP/-), but is still studied in several areas of the world due to growing population and inherent activities as agriculture, industry, energy production and transportation (Anatolaki and Tsitouridou 2009; Huang et al. 2010; Budhavant et al. 2011; Santos et al. 2011; Calvo et al. 2012, Izquierdo and Avila 2012; Wu et al. 2012; Al-Khashman et al. 2013; Facchini et al. 2014

). The chemistry of atmospheric deposition has historically been a fundamental matter of research, since closely linked to the atmospheric re-circulation of pollutants (acid rains, radioactive fallout) and their large-scale redistribution.

In general, atmospheric deposition reflects the same multi-source composition of aerosols potentially allowing to identify the influence of both anthropic and natural sources, such as industrial and human settlements, mobile sources, agricultural activities, sea spray, arid lands, etc. (e.g., Celle-Jeanton et al. 2009; Conradie et al. 2016; Roy et al. 2016). However, since a single chemical species frequently arises from multiple sources, its unique attribution to a given source is not straightforward. As an example, atmospheric dust and associated crustal elements (Ca^{2+}, Mg^{2+}, K^+) are originated by local sources (i.e., soil resuspension, mining and building operations), but can also be transported with air masses from desert regions distant from the collection site (Israelevich et al. 2002; Fraile et al. 2006; Kavouras et al. 2009; Shen et al. 2011; Creamean et al. 2013; Morales-Baquero et al. 2013). The fate of other components such as NO_2, SO_2 and NH_3 is even more complex, because their origin may be both primary (directly emitted by a given source to the atmosphere) and secondary, i.e., requiring an in-transit chemical formation step involving gas phase precursors and relatively slow chemical kinetics (Seinfeld and Pandis 2012).

In addition, the extent of wet removal depends not only on the pluviometric regime of the region investigated, but also on aerosol particle size typically ranging between the nanometer and the tenths of micrometers, particle composition, and hygroscopicity. It is highly variable and on average in the Po Valley (Northern Italy) it may range from about 50–60% for fogs (defined as occult deposition, Gilardoni et al. 2014) to 70% (Hicks et al. 1989) and even more.

This study provides an analysis of a five-year long time series of ion composition data, collected in bulk deposition from a semi-rural area of the Po Valley. This area is one of the most polluted in Europe (EEA 2013; Putaud et al. 2004) due to the high population density (more than 40% of the Italian population live in this region, while the surface represents about 34% of the national territory), in association with large industrial and human settlements, transportation, livestock and agricultural activities. Moreover, being almost completely surrounded by the Alps and the Apennines mountain chains, except in the eastern side facing the Adriatic Sea, atmospheric circulation over the Po Valley is very weak, promoting frequent stagnation conditions and atmospheric pollution build-up (e.g., Pernigotti et al. 2012). Due to public health and air quality constraints, most monitoring efforts in this area are presently devoted to gaseous and particulate pollutants, while, in spite of the relevance of nitrogen species fluxes with respect to large scale processes like eutrophication and acidification, the recovery of precipitation pH in Europe has contributed to a decrease of attention towards precipitation chemistry, which is presently much less monitored. Limited initiatives are active in this field in spite of large networks like EMEP. For this reason, this work has the scope of filling to some extent this gap, starting from a location in the heart of a highly-impacted area like the central Po Valley.

To this aim, local data on precipitation chemical composition are compared with results of other stations in the same district as well as with other locations worldwide. More-over, deeper insight on emission sources affecting composition over several time scales is obtained by basic statistical tools and multivariate analysis. Clusters of back-trajectories are also analysed to identify the origin of potential emission sources affecting precipitation composition.

2 Materials and methods

2.1 Sampling site

The study area is located in the Po Valley, Northern Italy. Bulk deposition sampling was carried out in the experimental farm of Cadriano of the University of Bologna (BO, 44°35′ N, 11°24′ E, 33 m a.s.l.[1]) (Fig. 1). Local climate is classified as temperate sub-continental ("C" following the widely used Köppen's classification -Köppen 1936-), with marked seasonal variations in both temperature and precipitation. The average temperature of the last 30 years (1983–2014) was 14.3 °C, with minimum values in January and maximum in July, while the average rainfall during the same period was 692 mm y^{-1}. Rainfall is mainly concentrated in two rainy seasons, spring and autumn, with relative maxima in April and November (Barrow and Hulme 1997).

The sampling site is located within a farm of 50 ha, where crops and orchards are cultivated following the typical agricultural practices of the region. In particular, fields are fertilized with nitrogen, potassium and phosphorus in different period of the year, depending on the cultivated species. The surrounding area is occupied by other cultivated areas and several anthropic sources of pollution: the farm lies about 9 km North of Bologna downtown (385.000 inhabitants), few km (1–5 km) far from industrial settlements, 4 km from the A13 highway, and 6 km from the Bologna municipal incinerator.

2.2 Chemical analysis

A total of 177 weekly bulk atmospheric depositions samples were collected in the period 2009–2013 by the rain gauge (33.5 cm polyethylene funnel fitted on a 15 l polyethylene bucket) of the agrometeorological station of Cadriano (Matzneller et al. 2010). The rain gauge was carefully cleaned with ultrapure water after sampling. On the day after collection, pH and electrical conductivity were measured by digital probes (Crison - pH meter GLP 22 and Conductimeter BasiC 30) following suitable calibration. After filtration through 0.4 μm nucleopore membranes, samples were stored at 4 °C in the dark before analysis performed typically within a week from the collection.

Bulk deposition was chemically characterized by means of the ion suppressed chromatography. The main cations (Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}) were analysed with a Dionex ICS-90 mounting a Dionex Ion Pack™ CS12A4x250 mm (Thermofisher) column with Dionex Ion Pac™ AG20 Guard Colunm 4 × 50 mm (Thermofisher) and Dionex CMMS™ 300 4 mm suppressor (Thermofisher), while anions (F^-, Cl^-, NO_2^-, NO_3^-, SO_4^{2-}, PO_4^{3-}) were determined with a Dionex ICS-2000 with an eluent generation system mounting Dionex EGC III KOH Eluent Generator Cartridge (Thermofisher), a Dionex Ion Pack™ AS11HC 2 × 250 mm (Thermofisher) column with Dionex Ion Pac™ AG11HC Guard Colunm 2 × 50 mm (Thermofisher) and Dionex AERS 500 2 mm suppressor (Thermofisher). Instrumental calibration was carried out using Multi-element standard solution for cations (Ca^{2+}; K^+; Mg^{2+}; Na^+), Multi-element IC Standard Solution for anions (F^-; Cl^-; SO_4^{2-}; NO_3^-; PO_4^{3}; NO_2^-) and Mono Element Calibration Solution for ammonium, all provided by CaPurAn. Ion calibration was based on 7 points obtained diluting suitably batch solutions in the range 0.1–50 ppm.
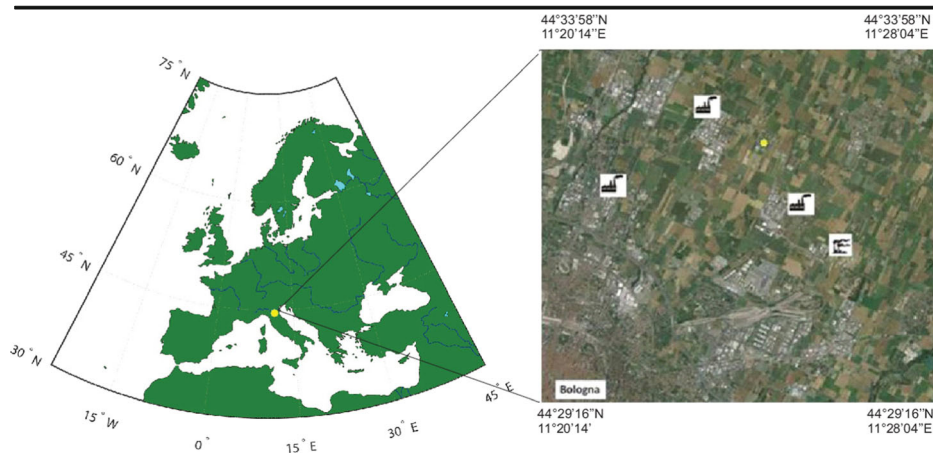
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[1] a.s.l. = above sea level

Fig. 1 Location of the sampling station (yellow symbol; 44°35′ N, 11°24′ E, 33 m a.s.l.) and nearby anthropogenic pollution sources (industrial settlement (⛏), incinerator (🏭), urban area of Bologna)

Experimental uncertainty was determined by 10 replicates of a suitable standard solution with a concentration level of ions enclosed within the calibration concentration range.

Detection limit (LOD) for each ion (see Table 1) was determined according to the expression:

$$LOD = X_b + 3\,(dev.std)_b$$

where X_b indicates the 5 points mean concentration measured in the blank, while $(dev.std)_b$ indicates its standard deviation.

2.3 Source identification

Since, as previously reported, ionic species in deposition (and in the scavenged aerosols) originate from multiple sources, and each source may emit several chemical species producing recognizable chemical fingerprints, the application of statistical analyses able to reveal the influence of specific sources at a receptor site is required. A high degree of association between environmental chemical species usually reveals common emission sources. Several statistical tools can be used to detect such associations. In this work basic statistics as well as multivariate statistical analyses were carried out to identify the factors which mostly affect the chemical composition of bulk deposition at this site. Moreover, to detect such associations, linear correlation and multivariate analyses, namely factor and cluster analysis, were carried out on

Table 1 Ions detection limits (in ppm). Between brackets we have reported detection limits expressed in $\mu eq\ l^{-1}$

Cations	Na^+	NH_4^+	K^+	Mg^{2+}	Ca^{2+}	
Detection limits (ppm)	0.02	0.04	0.05	0.01	0.11	
($\mu eq\ l^{-1}$)	(0.9)	(2.2)	(1.3)	(0.8)	(5.5)	
Anions	F^-	Cl-	NO_3^-	SO_4^{2-}	PO_4^{3-}	NO_2^-
Detection limits (ppm)	0.01	0.03	0.05	0.09	0.09	0.02
($\mu eq\ l^{-1}$)	(0.5)	(0.8)	(0.8)	(1.9)	(2.8)	(0.4)

the whole dataset. The Spearman correlation was preferred to Pearson model, due to the observed log-normality of data.

In particular, here we applied hierarchical cluster analysis with Ward's minimum variance method, where the distance between two clusters is the ANOVA sum of squares between the two clusters added up over all the variables, and using the squared Euclidean distances as metric (Wilks 2006). Furthermore, Varimax rotated (the most common of available rotations, scaling loadings by dividing them by the corresponding communality) factor analysis was also applied (Wilks 2006). Prior to the application of multivariate statistical analyses, data below the LOD were substituted with LOD/2, and the whole matrix was standardized.

Moreover, we also calculated marine and crustal enrichment factors (EF) to identify the sources of ions in rainwater (Arsene et al. 2007; Zhang et al. 2007). Marine enrichment factors were calculated using Na^+ as reference ion for marine source, assuming it to be of solely marine origin and highly conservative (Kulshrestha et al. 2003), while crustal enrichment was calculated using Ca^{2+} as reference ion for elemental crust (Zhang et al. 2007).

Enrichment factors were calculated using the following formulae (Zhang et al. 2007):

$$EF_{\text{seawater}} = \left[X \middle/ Na^+\right]_{\text{rainwater}} \middle/ \left[X \middle/ Na^+\right]_{\text{seawater}}$$
$$EF_{\text{crust}} = \left[X \middle/ Ca^{2+}\right]_{\text{rainwater}} \middle/ \left[X \middle/ Ca^{2+}\right]_{\text{crust}}$$

Where X is the concentration of the ion of interest, X/Na^+ of seawater is the ratio from seawater composition (Riley and Chester 1971), and X/Ca^{2+} of crust is the ratio from crustal composition (Taylor, 1964). In general, EF much less (higher) than 1 suggest a dilution (enrichment) relative to the reference source (Zhang et al. 2007).

The relative neutralization actions of Ca^{2+}, NH_4^+, and Mg^{2+} were examined by calculating the neutralization factor $NF_x = X / \left(SO_4^{2-} + NO_3^-\right)$ (Kulshrestha et al. 2003), where X is the concentration ($\mu eq\ l^{-1}$) of the ion of interest.

Statistically significant differences were checked using t-test, sign test, and Wilcoxon test with a significance level (p) of 0.05.

Moreover, in order to study the influence of air masses on the chemical precipitation in the sampling site, for each rainy sampling day in Cadriano five days long 3D back-trajectories were calculated at three different altitudes (500, 1500, and 3000 m a.s.l.) and four times a day (00, 06, 12, 18 UTC). Back-trajectories were calculated with the HYbrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT, version 4.9) model (Draxler et al. 2014), using the GDAS (Global Data Assimilation System) meteorological database (1° latitude-longitude resolution, 23 pressure levels from 1000 to 20 hPa, 3 h temporal resolution). In this case, the consideration of only rainy days was done to better distinguish wet from dry deposition occurred during the sampling of bulk deposition.

The cluster technique implemented in the HYSPLIT model was used to obtain clusters of back-trajectories. In fact, statistical classification approaches aggregating a large number of trajectories calculated over a long-lasting period tend to average out the limitations and uncertainties affecting individual back-trajectories, deriving from the meteorological fields, the interpolation to trajectory positions and the lack of representation of small-scale effects (Stohl 1996). The grouping module of HYSPLIT is based on variations in the Total Spatial Variance (TSV) between different clusters, to be compared to the spatial variance (SPVAR) within each cluster component (Draxler et al. 2014). The final number of clusters is determined by a change in TSV, and in particular by the first variation of the TSV above 30%.

Considering that our database of chemical composition of bulk deposition consisted of weekly, while we had 4 trajectories for each rainy day, we needed a criterion to statistically associate each weekly observation with obtained clusters of back-trajectories: in our case, one weekly observation was attributed to one cluster only if at least 60% of the associated trajectories belonged to that particular cluster.

2.4 Quality data assessment

Analytical quality control was carried out analysing the following certified reference materials (CRMs) Fluka Multielement Ion Chromatography Cation Standard Solution certified (cod. 89,316-50 ml-F) and Fluka Multielement Ion Chromatography Anion Standard Solution certified (cod. 89,886-50 ml-F). The certified values of ion concentration, the mean concentrations experimentally obtained in the Environmental Chemistry and Radioactivity Lab of the Dep. Of Chemistry "G. Ciamician" of the University of Bologna as a result of 20 replicates, their respective uncertainties and the mean percent deviation of experimental from certified values are reported in the SI (SI Table 1). All the data obtained were below the 5% deviation from the certified values of the CRM's used.

A further quality check of the data was performed comparing measured and calculated conductivities, a parameter dependent on the total dissolved solids. Calculated conductivities were estimated summing up the concentrations (in ppm) of all determined ions and multiplying the result by two. If all major ions of the solutions are measured, then the conductivity of the total ions must be approximately equal to the conductivity of the solution measured by a conductivity meter. As shown in Fig. 2a measured and calculated conductivities showed a good correlation ($R^2 = 0.89$, $p < 0.05$), indicating that the majority of ions was detected. Nevertheless, when the sum of anion equivalents is checked against cation equivalents, an anion deficit is found, in spite of a good linear correlation ($R^2 = 0.88$, $p < 0.05$) between the two parameters (Fig. 2b).

In the absence of alkalinity measurements as in the present work and in agreement with atmospheric chemistry this unbalance is usually attributed to carbonates/bicarbonates which are the typical counterions of Ca^{2+} and Mg^{2+} (e.g., Khoiyangbam 2005), which are fairly abundant in our samples. This hypothesis is supported by the previous findings of Pieri et al. (2010), reporting mean carbonate levels in the range of 39–62 $\mu eq \, l^{-1}$ in two sites in the Po Valley relatively close to Cadriano, in agreement with acid base chemistry in southern Europe regions (Al-Momani et al. 1995; Tuncer et al. 2001).

As previously described, the adopted sampling setup collects both wet and dry deposition, and is likely affected by soil resuspension and, to a lesser extent, by Saharan dust incursions, which are observed in this region not only in the form of precipitation but also in the "dry" suspended form, affecting therefore the local aerosol population.

Once discarded analytical artefacts, thanks to rigorous laboratory quality control, data were carefully analysed to characterize the behaviour of atmospheric deposition at the sampling site.

3 Results and discussion

Since meteorology undergoes strong inter-annual variations and climate change is likely to play a significant role in this respect, precipitation data recorded during the investigated period were analysed in detail based on a comparison with climatological means. In this area,

Fig. 2 Scatterplot of **a** measured vs. calculated electrical conductivity (EC), and **b** anions sum vs. cations sum (in eq l^{-1} units)
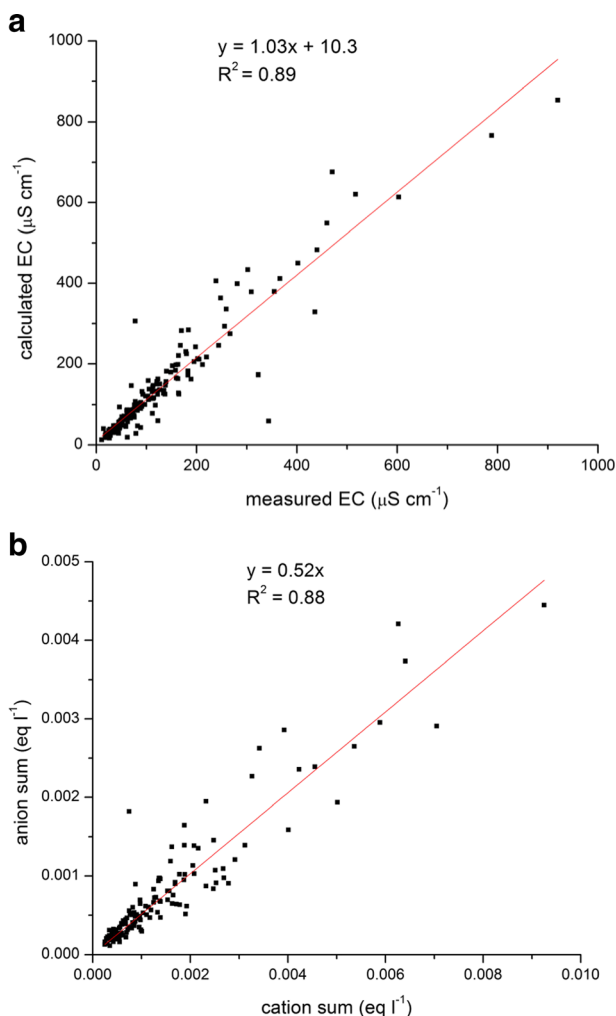
precipitation is usually characterized by an absolute maximum in November and a secondary maximum in April, linked to the transition from the Azores high pressure in summer to the Siberian low pressure in winter (Barrow and Hulme 1997). This bi-polar annual behaviour, typical of the Mediterranean climate, leads to pressure lows in autumn and spring, which are therefore characterized by frequent precipitation, often under the strong influence of Genoa cyclogenesis. In agreement with what mentioned above, the precipitation seasonal pattern observed in Cadriano during the 2009–2013 investigated period was characterized by the presence of an autumn maximum and a secondary spring maximum.

Annual precipitation recorded during the sampling period 2009–2013 ranged between the minimum of 453 mm y^{-1} in 2011 and the maximum precipitation of 921 mm y^{-1} in 2013, with a 5 years mean of 719 mm y^{-1}. The 5 years average is not statistically significant ($p >> 0.05$) different from the climatological means of the periods 1961–1990, 1971–2000, 1952–2014, 1983–2014 (723, 703, 742, and 692 mm y^{-1}, respectively) (Bagnouls and Gaussen 1953, 1957). The comparison of single years highlighted an anomaly in 2011, which was statistically

significantly drier, both compared to climatological data and to the other years analysed in the present work ($p < 0.05$ in all cases).

3.1 Back-trajectory analyses

Back-trajectories were calculated at three different heights (500, 1500, and 3000 m a.s.l.) to better represent local meteorology and different types of precipitation (stratiform vs. convective). Three clusters of back-trajectories (available as Supplementary Material, hereafter SI, Fig. 1SI) were identified at each height, namely Eastern (E), Southern (S), and Western (W), with minor differences in the location of the cluster centers among the different heights. The main difference is the displacement of the S cluster towards W with height.

The location of the cluster centers corresponds to the main directions of provenance of the cyclones in Cadriano, mostly affected by cyclones developing south of the Alps in the Gulf of Genoa, Ligurian Sea, Po Valley, Gulf of Venice and northern Adriatic Sea. As known, all these cyclones are grouped together in the "Genoa low" category, and the development of the cyclone near the Gulf of Venice or to the west near the Gulf of Genoa depends on the amount of cold air penetrating the Po Valley from the northeast: cyclogenesis occurs in the Gulf of Venice when only little or no cold air enters the Po Valley (Reiter 1971).

While the frequency of W trajectories is constant with height, that of E trajectories gradually decreases with height, being replaced by S (SW, i.e. South-Western) trajectories which are more frequent at upper heights.

The seasonality of the three clusters (Fig. 3) corresponds to the seasonality of the main synoptic disturbances in Cadriano, and generally speaking in Northern Italy. Notwithstanding the differences among the three heights, it is clear that E trajectories are more common during the cold period, W trajectories prevail during the transition and warm period, and finally S trajectories prevail only at 3000 m a.s.l. and are more frequent during the transition season and late summer (August).

The interannual variations of the frequency of the three clusters of back-trajectories (Fig. 2SI) explains the reduced precipitation observed in 2011 as resulting from the marked reduction in the frequency of W advections in 2011, clearly noticeable at all the three heights and probably linked to a reduced frequency of Genoa cyclogenesis in Cadriano during that year.

3.2 General features of bulk deposition chemistry

Basic statistics (mean, median, maximum and minimum values) of pH, measured electrical conductivity (EC), cations and anions in bulk deposition samples in the five-year period are reported in Table 2. The average and maximum values for EC were 117 μS cm^{-1} and 920 μS cm^{-1}, revealing that the collected bulk deposition samples were very concentrated in chemical species, especially considering that the sampler was located in a semi-rural area. These high EC values might be linked both to the adopted sampling methodology (weekly bulk deposition), as well as to the location of the sampling site close to agricultural activities, industrial areas and urban settlements.

The dataset shows a wide range of concentrations for each ion over the sampling period. As highlighted by the minimum and maximum values (Table 2), the concentration of the major ions varied over more than four orders of magnitude. The mean concentrations of the anions (in μeq l^{-1}) can be arranged in a descending order as follows: NO_3^- (243) > SO_4^{2-}

Fig. 3 Monthly variation of the frequencies (%) of clusters of back-trajectories (2948 total back-trajectories; E = Eastern, S = Southern, W = Western) identified at **a** 500 m a.s.l.; **b** 1500 m a.s.l.; **c** 3000 m a.s.l
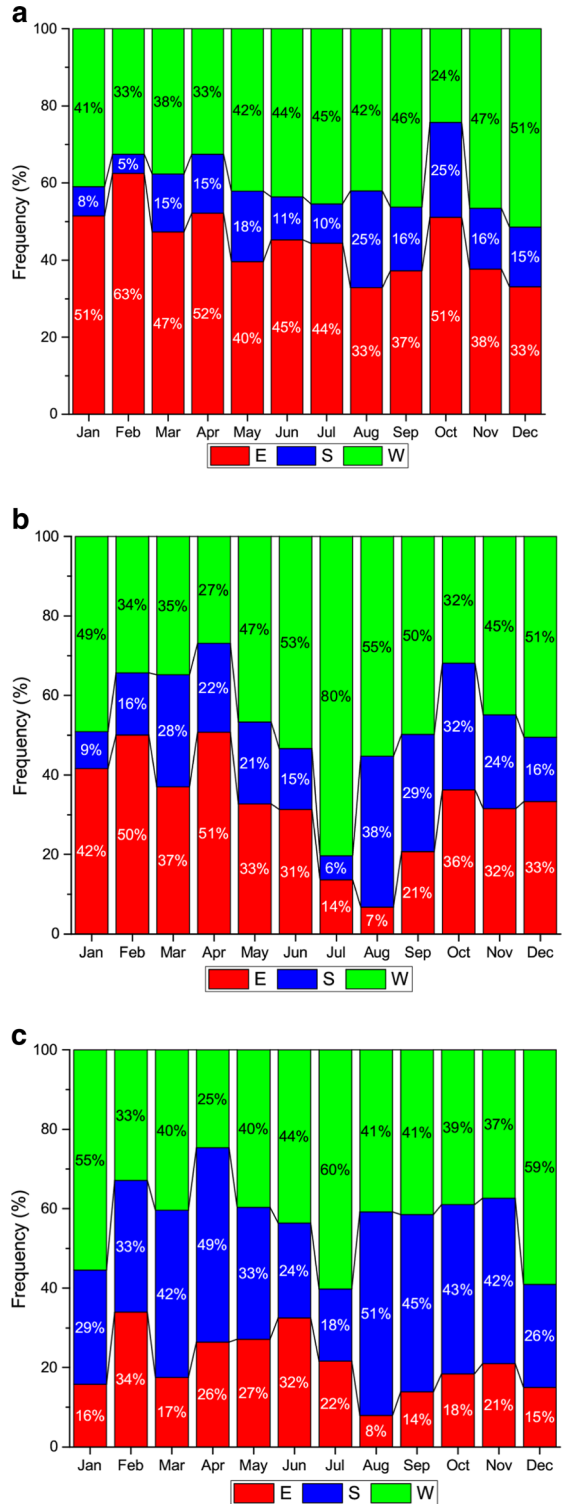
Table 2 Basic statistics for experimentally determined values of pH, EC (electrical conductivity; in $\mu S\ cm^{-1}$), and ions ($\mu eq\ l^{-1}$) in 177 bulk samples collected in Cadriano in the period 2009–2013. Mean is the arithmetic mean of the samples. Min = minimum; Max = maximum; Std.Dev. = standard deviation

	Mean	Median	Min	Max	Std.Dev.
pH	7.0	7.1	5.8	8.4	0.5
EC	117	78	5.8	920	119
Na^+	127	80	2.5	1896	185
NH_4^+	504	253	4.8	3532	677
K^+	151	34	1.3	2291	311
Mg^{2+}	124	63	10	1056	162
Ca^{2+}	489	341	32	4196	510
F^-	2.6	1.6	0.5	148	3.1
Cl^-	153	90	6.5	1377	210
NO_2^-	29	10	0.6	546	59
NO_3^-	243	125	1.3	2796	338
SO_4^{2-}	220	120	15	1526	270
PO_4^{3-}	176	37	3.1	3133	352

$(220) > PO_4^{3-}\ (176) > Cl^-\ (153) > NO_2^-\ (29) > F^-\ (2.6)$. The concentration of cations (in $\mu eq\ l^{-1}$) follow the general pattern: $NH_4^+\ (504) > Ca^{2+}\ (489) > K^+\ (151) > Na^+\ (127) > Mg^{2+}\ (127)$.

The frequency distribution of each chemical parameter was analysed (Fig. 4 and Fig. 3SI). As highlighted in Fig. 4, the pH, as a logarithmic variable, does not show strong asymmetries in its frequency distribution, presenting a major peak between 7.0 and 7.2 which shows the tendency toward slightly alkaline conditions. A further evaluation of frequency distribution on a seasonal basis shows that pH is bi-variate in all seasons (northern Hemisphere definition: winter, spring, summer, autumn) except in summer (not shown). The highest pH values were recorded in summer (mean pH = 7.2 ± 0.5), while slightly lower values were recorded in the other seasons: spring, autumn and winter mean values with standard deviations were respectively equal to 7.0 ± 0.6, 7.0 ± 0.4 and 7.1 ± 0.5.

Fig. 4 Frequency distribution of pH analysed in bulk deposition samples of Cadriano
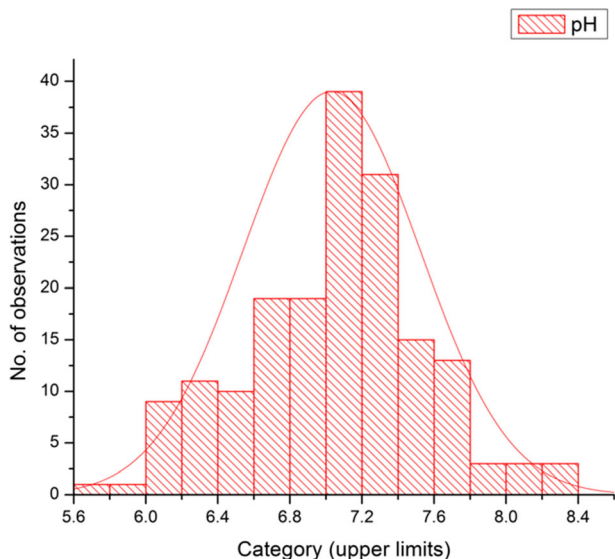
The hydrometeors pH, normally ranging between 5 and 5.6, may be affected by the concentration of H_2SO_4 and HNO_3 and to a lesser extent by carboxylic species (typically minor components in aerosols -Kawamura and Ikushima 1993; Mader et al. 2004-), all reflecting their connection with gas-to-particle conversion chemistry which in turn is affected by wet scavenging. In this framework ammonia is usually the main alkaline agent leading to a final neutralization degree leading to the detected ammonium resulting from the neutralized acid fractions. Physico-chemical definition of pH applies to solutions which means for example rainwater, snow melt water, fog water, seawater, ... As for aerosols which are not solution and whose physical state is uncertain ranging from a suspension of particles to droplets, the definition of pH does not apply and only an extrapolated H^+ concentration can be deduced by balancing cations and anions experimentally determined. pH values observed in bulk deposition are in good agreement with present day pH of airborne particulate in this area (as evaluated from the equivalence ratio between the experimental concentration of $nssSO_4^{2-}$, NO_3^- and NH_4^+ in aerosol samples, Tositti et al. 2014 and references therein), where aerosol is mostly neutralized due to mitigation strategies in Europe in the last decades and to ammonia availability.

The alkaline pH of the bulk depositions of Cadriano, in spite of high concentrations of nitrates and sulphates, is attributed to the large presence of neutralizing agents such as ammonium, but also to alkaline-earth crustal elements. In particular, the relevant concentrations of crustal elements suggest a possible link of alkaline conditions with correspondingly high concentrations of carbonates/bicarbonates in our dataset, whose direct measurement was not possible as previously explained in the paragraph concerning the quality data assessment. Thus, the highest value in summer can be explained considering soil resuspension, important source of crustal element (Ca^{2+}, Mg^{2+}, K^+) in rural areas, resulting from low level turbulence especially during the dry season, due to mechanical operations in the cultivated fields and in agreement with aerosol properties measured in this region in the warm season (Tositti et al. 2014; Putaud et al. 2004). A similar behaviour was also observed by Budhavant et al. (2011) and Izquierdo and Avila (2012), analysing the chemical composition of bulk deposition samples collected in India and in North-Eastern Spain, respectively. Soil resuspension brings about an increase of Ca^{2+} and Mg^{2+} coupled with carbonates which provide further neutralization of aerosol-derived acidic species. As a result, the smaller secondary maximum at slightly lower pHs is not found in summer subset.

In fact, the calculation of neutralization factors indicated that Ca^{2+} and NH_4^+ are by far the dominant neutralization components in rainwater in Cadriano (average NF equal to 1.5 and 1.4, respectively, as compared to the average NF of Mg^{2+} equal to 0.3).

As shown in Fig. 3SI, differently from pH, on average ions display a log-normal distribution, with a highly-populated mode at lower concentrations and smaller peak values at higher concentrations. This indicates that the median better represents our data, even if the arithmetic mean is to be used for comparison with literature data.

Figure 5 shows boxplots describing the interannual variability of precipitation chemistry during the investigated period. The reported boxplots reveal that the highest ion concentrations were recorded during the 2011 and 2012 years, while year 2009 presented on average the lowest ion concentrations along the investigated period. Analysis of significant differences was applied to infer potential differences in precipitation chemistry in the studied years. This approach confirmed that the higher concentration in alkali and alkaline earth species in 2011 samplings are statistically
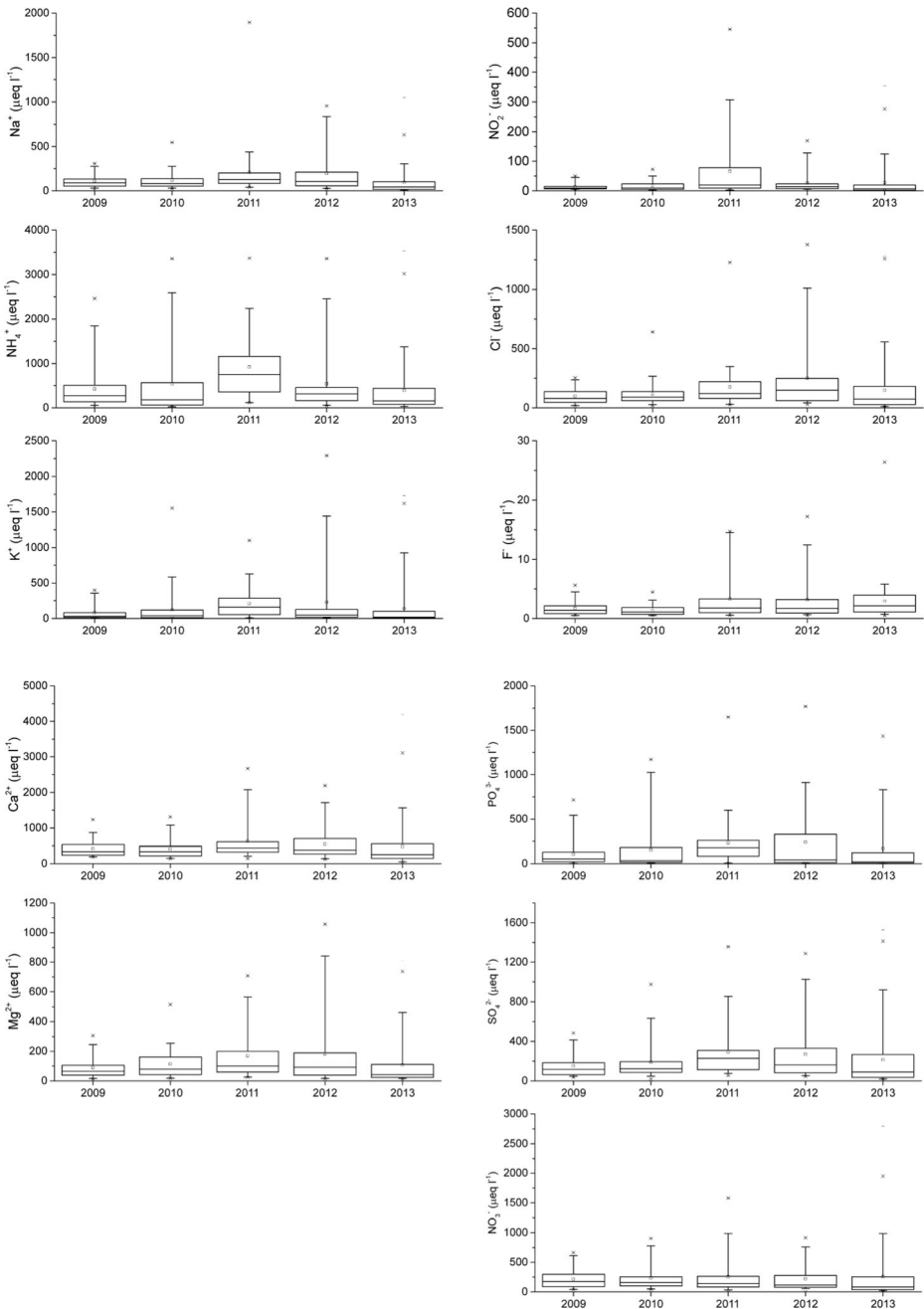
Fig. 5 Boxplots showing the interannual variability in the 2009–2013 period at the Cadriano site. The boxes contain the 25th–75th percentile of the data; the whiskers represent the 5th and 95th percentile, while the square and the line inside the boxes denote the arithmetic mean and the median, respectively. Crosses and external lines represent the 1st-99th percentiles and extreme values (minima and maxima), respectively

significant in agreement with the drier climatic conditions of the year and with the consequently enhanced soil resuspension.

3.3 Monthly and seasonal pattern

Figure 6 depicts the monthly pattern of the main ions. Most of the ions present September peaks, and higher values during the summer months, again likely linked to the effect of enhanced dry deposition and to the higher soil resuspension during this season. Among cations, NH_4^+ shows the highest concentrations from May to September. This behaviour was also observed in Spain (Calvo et al. 2012) and may be due to: a) the increased availability of atmospheric ammonia mostly released by the agricultural practice and especially manure
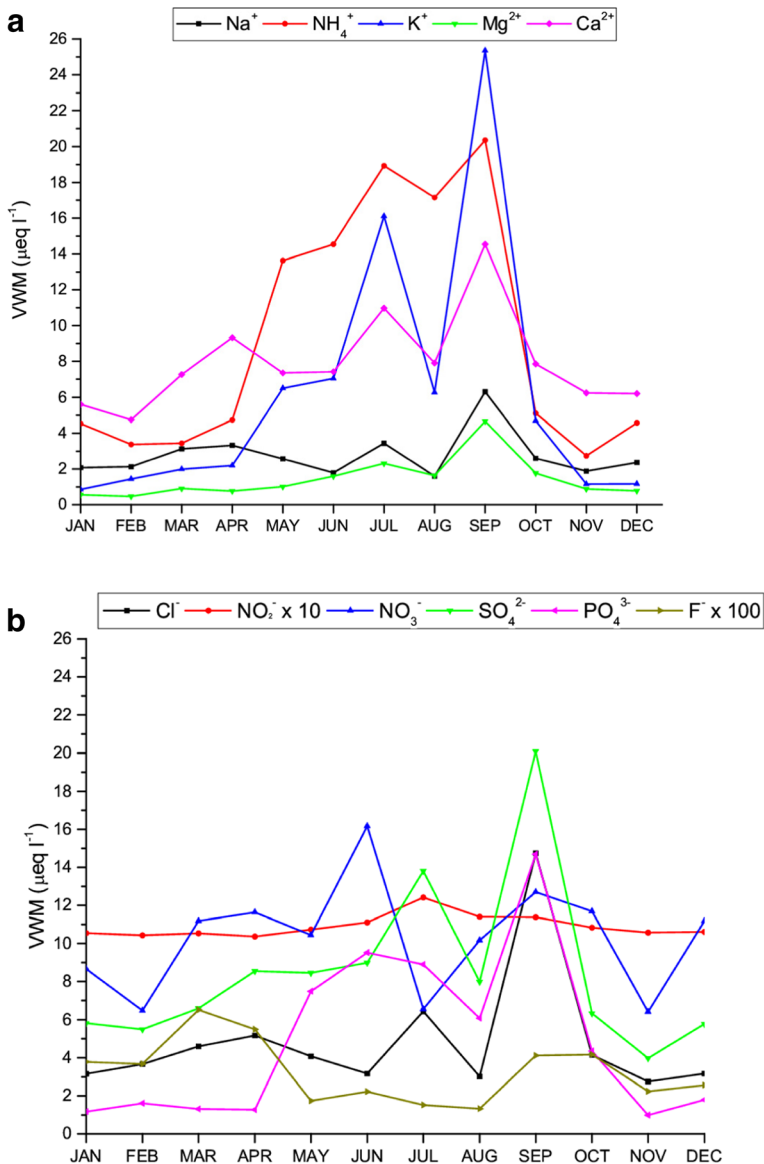

Fig. 6 VWM monthly concentration of cations (**a**) and anions (**b**) in samples of bulk deposition

management and agricultural soils; b) higher NH_3 emissions with high summer temperature and remarkable reactivity of this alkaline gas which is rapidly scavenged by water and by gas to particle conversion reactions (Van Damme et al. 2015). It is to note here that ammonium nitrate presents a low stability at high temperatures (e.g., Schaap et al. 2004).

The role of agriculture in the ammonia emission was also emphasized by Reche et al. (2015), who suggested that the occurrence of NH_3 in the atmosphere is firstly due to decomposing livestock waste, and secondarily to losses from vegetation and agricultural fields, as a result of the application of N fertilizers. As a whole, agriculture is responsible of about 93% of total NH_3 emission in Europe (EEA 2015). Therefore, the high concentration of ammonium recorded in Cadriano is likely due to agricultural activity, and in particular to the nitrogen fertilizations that are carried on from January to May as urea or ammonium nitrate, as a function of crop rotation.

As reported in Fig. 6, the monthly pattern of crustal elements, and in particular Mg^{2+}, Ca^{2+} K^+, shows higher concentrations in summer, while Na^+ remains pretty constant during the year. As already observed by Migliavacca et al. (2005), elevated amounts of crustal elements are expected during the hot season as a result of their higher concentration in airborne particulate matter and its removal (wet and dry).

Anions present reduced seasonal variations with respect to cations. PO_4^{3-} shows a peak in September and higher summer values, likely reflecting use of phosphate fertilization typical of the period. SO_4^{2-} shows a peak in September and higher summer values. This behaviour can be explained by the more efficient oxidation chemistry of SO_2 (e.g., Vecchi et al. 2004); the sulphates maximum in September can be influenced by: 1) Saharan dust events which includes also gypsum i.e. $CaSO_4$ (Claquin et al. 1999); 2) soil resuspension since soils of the area investigated are characterized by a gypsum intrinsic component as derived by local soil genesis (http://geo.regione.emilia-romagna.it/cartpedo/; Emilia-Romagna et al. 1994); 3) sulphate contribution from agricultural management.

NO_3^- presents peaks in June and September, with minima recorded in July and August. This behaviour is probably linked to the use of N fertilizations in the area, typically carried on three times in June on all the cultivations. Cl^- presents a September maximum, that, given the presence of the contemporary Na^+ peak in the same month, is probably linked to the higher frequency of frontal situations occurring over marine surfaces, as suggested by the higher frequency of W trajectories observed in Fig. 3.

Finally, F^- and especially NO_2^- present less marked intramonth variation with respect to other ions, with the presence of a small F^- peak in March and a very small NO_2^- peak in July.

3.4 Comparison with other locations

Table 3 shows the comparison among the chemical composition in bulk deposition of Cadriano with the one obtained in other worldwide locations, including sites close to Cadriano with a parallel monitoring activity.

Mean ion concentrations from Cadriano are higher compared to other sites recently monitored, both concerning acidic and alkaline species (Migliavacca et al. 2005; Demirak et al. 2006; Balestrini et al. 2007; Anatolaki and Tsitouridou 2009; Huang et al. 2010; Budhavant et al. 2011; Lu et al. 2011; Santos et al. 2011; Calvo et al. 2012; Đurašković et al. 2012; Izquierdo and Avila 2012; Pieri et al. 2010, 2012; Wu et al. 2012; Al-Khashman et al. 2013). Only the urban Chinese site described by Lu et al. (2011) presents higher and/or comparable concentrations of the main chemical species. SO_4^{2-} 490 µeq l^{-1}, NO_3^- 129 µeq l^{-1},

Table 3 Concentration of major ions analysed in bulk deposition of Cadriano expressed as annual volume weighted mean (VWM) compared to various location worldwide (µeq l⁻¹)

Site	U-R-SR-C*	Reference	Sampling period	pH	NO_3^-	SO_4^{2-}	Cl^-	Na^+	Ca^{2+}	NH_4^+	K^+	Mg^{2+}
Italy	SR	Cadriano, present study	Jan 2009 – Dec 2013	7.0	178	190	153	150	407	523	162	120
Italy	R	Pieri et al. 2012	Feb 1997- Jan 2000 Jan 2007-Jan 2010	6.3	66	78	65	48	185	n.a.	n.a.	59
Italy	U	Pieri et al. 2012	Feb 1997- Jan 2000 Jan 2007-Jan 2010	6.2	37	58	49	122	160	n.a.	n.a.	54
Italy	U	Pieri et al. 2010	Feb 1997 – Jan 2000	5.1	67	118	106	96	122	58	34	20
Italy	R	Pieri et al. 2010	Feb 1997 – Jan 2000	5.3	89	104	88	83	137	82	23	19
Italy – EM**	R	Balestrini et al. 2007	1999–2003	-	49	49	22	22	50	65	4	9
Italy-PIE**	R	Balestrini et al. 2007	2002–2004	-	33	27	8	9	20	36	3	4
Italy-LOM**	R	Balestrini et al. 2007	1997–2000	-	22	30	6	6	26	24	2	4
Italy-FRI**	R	Balestrini et al. 2007	2001–2003	-	22	26	10	11	25	23	3	8
Italy-LAZ**	R	Balestrini et al. 2007	2000–2003	-	29	42	57	54	79	20	5	17
Portugal	U-R-C	Santos et al. 2011	Sep 2008- Sep 2009	4.5–6.9	28	24	145	n.a.	n.a.	13	n.a.	n.a.
Montenegro	C	Đurašković et al. 2012	Jan 1995 – Dec 2000	6.0	32	116	113	107	97	27	14	81
Greece	U	Anatolaki and Tsitouridou 2009	Apr 2002 – Mar 2004	6.6	41	134	57	45	256	116	16	31
Spain	R-C	Izquierdo and Avila 2012	Feb 2009 – Jul 2010	6.5	23	20	16	13	38	22	3	6
Spain	R	Calvo et al. 2012	Jan 2002 - Dec 2006	6.7	22	27	22	18	77	32	3	16
Turkey	U	Demirak et al. 2006	Feb 2002 – Apr 2002	6.7	30	131	n.a.	40	298	32	7	n.a.
Jordan	R	Al-Khashman et al. 2013	Oct 2006 – May 2011	7.1	32	40	73	70	125	26	15	60
India	U-R	Budhavant et al. 2011	2006–2009	5.8–6.7	13	35	45	40	62	10	n.a.	n.a.
China	U	Huang et al. 2010	2005–2009	4.6	22	65	21	11	35	34	n.a.	n.a.
China	U-R	Wu et al. 2012	Mar 2008 – Oct 2008	5.4	17	152	n.a.	11	156	33	9	n.a.
China	U	Lu et al. 2011	Mar 2010 – May 2010	6.6	129	490	39	31	426	230	14	37
Brazil	U	Migliavacca et al. 2005	Jan 2002 – Dec 2002	5.8	16	14	17	25	40	21	7	24

*R rural, SR semirural, U urban, C coastal

**EM Emilia-Romagna region, PIE Piemonte region, LOM Lombardia region, FRI Friuli-Venezia Giulia region, LAZ Lazio region (names of the sampling sites in the original manuscript)

n.a. not available

Ca^{2+} 426 µeq l^{-1}, NH_4^+ 230 µeq l^{-1}, and SO_4^{2-}190 µeq l^{-1}, NO_3^-178 µeq l^{-1}, Ca^{2+} 407 µeq l^{-1}, NH_4^+ 523 µeq l^{-1} were respectively the ions concentrations in the Chinese site and in Cadriano. Some of the differences of rainwater ion composition analysed at Cadriano with that analysed at other sampling sites may depend on the different sampling period and different changes in precipitation chemistry (Vet et al. 2014).

However, the comparison of the cations concentration recorded in Cadriano only with other sites in the Mediterranean basin clearly shows that all this area is characterized by high concentration of crustal elements, especially calcium, which leads the pH toward alkaline conditions (Table 3). This result probably depends from the fact that all the Mediterranean sites are characterized by calcareous soils, subjected to resuspension in dry period, and/or are reached by Saharan dust.

The ion concentrations are also higher when compared to the other two sites of the same district of Cadriano (one rural and one urban) monitored by the authors (Pieri et al. 2010) during the same period at least partially (2009), as well as to other Italian forested sites (Balestrini et al. 2007). Indeed, these differences are probably due to the diverse density of local source pollutions. Thus, the rural site described in Pieri et al. (2012), even if only 15 km distant from Cadriano, is at an altitude of 180 m a.s.l. next to the Po Valley, far from industrial and urban settlements. The area is mainly occupied by spontaneous vegetation and organic farming, which constitutes the local source of pollution. The Italy-EM site, described in Balestrini et al. (2007), is a forested site located next to the Po Valley at an altitude of 200 m a.s.l., far from sources of pollution.

As previously noted the main neutralization components in rainwater in Cadriano are calcium and ammonium. Calcium is also the major neutralization component at most of other Mediterranean sites (Demirak et al. 2006; Italy-LAZ from Balestrini et al. 2007; Anatolaki and Tsitouridou 2009; Calvo et al. 2012; Izquierdo and Avila 2012; Pieri et al. 2010, 2012; Đurašković et al. 2012; Al-Khashman et al. 2013) and worldwide (Migliavacca et al. 2005; Budhavant et al. 2011; Wu et al. 2012), while ammonium is also the main neutralization component at Italy-EM and Italy-PIE (Balestrini et al. 2007).

The ion concentrations (especially the elevated concentration of ammonium) together with these comparisons suggest that probably the farm activity constitutes the main source of pollution, even if probably affected also by the nearby presence of a large number of industrial and residential settlements (Fig. 1).

3.5 Analysis of ions sources

Results of the Spearman correlation are provided in Fig. 7 together with scatter plots are presented. High values of the correlation coefficient ($R > 0.7$) suggest a large degree of association (covariance) between couples of parameters, while intermediate values of the correlation coefficient (R in the range 0.4–0.6) mean that the correlation may still exist but can be complex. Finally low values ($R < 0.4$) indicate a potential lack of correlation between the parameters. In this case, high values are found in a limited number of cases, while, excluding the cases with low R characterized by very scattered data, it is possible to observe (Fig. 7) the presence of two or more clusters of data in several scatter plots (Na+-NH4+, Na+-K+, Na+-NO2−; NH4+-K+, NH4+-Ca2+, NH4+-NO3−; K+-Ca2+; Ca2+-PO43− F−-PO43−; Cl−-NO2−). Even though interpreting the existence of these clusters in a data set is often difficult, this finding might indicate the multiplicity of source of pollutions and is probably also due to the complexity of precipitation formation.
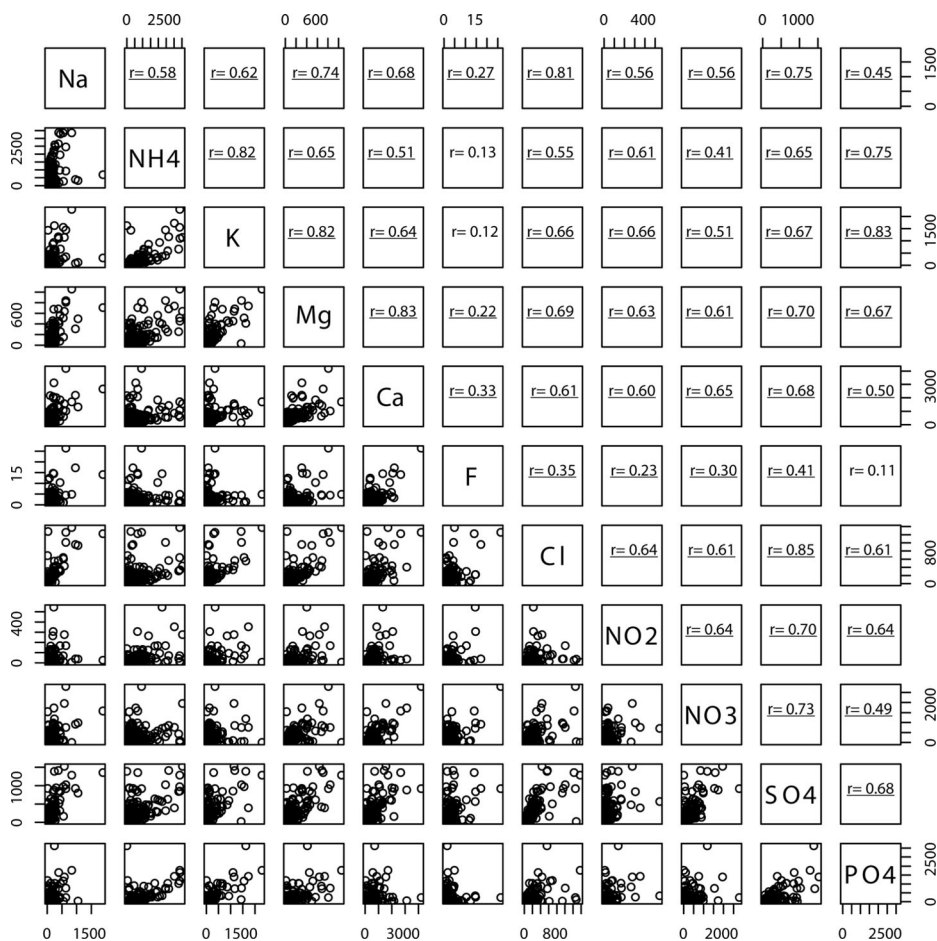
Fig. 7 scatterplot matrix — axis ranges and Spearman's rank correlation coefficients:

Axis ranges (top): 0 2500 | 0 600 | 0 15 | 0 400 | 0 1000

	Na	NH4	K	Mg	Ca	F	Cl	NO2	NO3	SO4	PO4
Na	Na	r= 0.58	r= 0.62	r= 0.74	r= 0.68	r= 0.27	r= 0.81	r= 0.56	r= 0.56	r= 0.75	r= 0.45
NH4		NH4	r= 0.82	r= 0.65	r= 0.51	r= 0.13	r= 0.55	r= 0.61	r= 0.41	r= 0.65	r= 0.75
K			K	r= 0.82	r= 0.64	r= 0.12	r= 0.66	r= 0.66	r= 0.51	r= 0.67	r= 0.83
Mg				Mg	r= 0.83	r= 0.22	r= 0.69	r= 0.63	r= 0.61	r= 0.70	r= 0.67
Ca					Ca	r= 0.33	r= 0.61	r= 0.60	r= 0.65	r= 0.68	r= 0.50
F						F	r= 0.35	r= 0.23	r= 0.30	r= 0.41	r= 0.11
Cl							Cl	r= 0.64	r= 0.61	r= 0.85	r= 0.61
NO2								NO2	r= 0.64	r= 0.70	r= 0.64
NO3									NO3	r= 0.73	r= 0.49
SO4										SO4	r= 0.68
PO4											PO4

Axis ranges (right): 0 1500 | 0 1500 | 0 3000 | 0 800 | 0 2000 | 0 2500
Axis ranges (left): 0 2500 | 0 600 | 0 15 | 0 400 | 0 1000
Axis ranges (bottom): 0 1500 | 0 1500 | 0 3000 | 0 800 | 0 2000 | 0 2500

Fig. 7 Lower panel, left from the diagonal: scatterplots of the ions ($\mu eq\ l^{-1}$) analysed in the weekly bulk deposition samples collected in Cadriano. Upper panel, right from the diagonal: Spearman's rank correlation coefficient values for ionic composition in Cadriano in 2009–2013. Significant correlation coefficients ($p < 0.05$ significance level) are underlined

Prior to the application of multivariate statistical analyses, the calculation of marine and crustal enrichment factors was used to infer the potential sources of ions in our dataset (Table 4): the high EFs calculated for fluorides (crustal EF > > 10), NO_3^-,(crustal EF > > 10), SO_4^{2-} (both crustal and marine EF > 10) suggest their likely anthropogenic origin, while K^+ and Mg^{2+} resulted enriched with respect to seasalt (marine EF > 10 for both species) but diluted with respect to the Earth's crust (crustal EF < 1 for both species).

Both the multivariate analyses, namely cluster (Fig. 8) and factor analysis (Table 5), largely agree in terms of associations of parameters. In particular both methodologies yield and emphasize the association between NH_4^+, K^+ and PO_4^{3-}, which together explain 51% of the total variance of the dataset in the factor analysis (Factor 1, Table 5), indicating an overwhelming influence of this factor on the deposition chemistry at this site. This group strongly suggests an influence from agricultural practice, in terms of fertilization, in the surrounding of the sampling station as a result of the sampling method adopted (bulk deposition), enabling the

Table 4 Marine and crustal enrichment factors (EF) calculated using Na^+ as reference ion for seawater, and Ca^{2+} as reference ion for elemental crust

	EF_{marine}	Ef_{crust}
Cl^-	1.2	147
SO_4^{2-}	11	30
Mg^{2+}	11	0.4
K^+	38	0.6
Ca^{2+}	186	–
F^-	621	–
NO_3^-	–	273

collection of resuspended/recirculated particles from the terrain around. In fact, studies of aerosols in this region highlights that, differently from the present study, PO_4^{3-} is only a minor component, often below the detection limits (as observed in Tositti et al. 2014, it was detected only in 19% of the cases, and on average it contributed only to the 0.2% of PM_{10} mass fraction), while NH_4^+ is typically strongly correlated with NO_3^- and SO_4^{2-} as a result of the well-known gas-to-particle reactions from precursor gases, followed and/or accompanied by water nucleation in cloud processing (Finlayson-Pitts and Pitts 2000; Seinfeld and Pandis 2012). Even though factor analysis further associates SO_4^{2-} and Mg^{2+}, which appear also in the third factor, this grouping yielded independently by two different statistical methods enforces the interpretation provided above.

Factor 2 associates Na^+ to Cl^- (Table 5), which are also strongly correlated and clearly solved in cluster analysis (Fig. 8), pointing out the importance of marine salt, a natural component of aerosol which could be invoked in cloud/precipitation formation when frontal conditions are promoted by circulation over marine surfaces (Atlantic, Tyrrhenian sea; Gulf of Genoa, Gulf of Trieste), as local climatology suggests. This factor also comprehends fluorides, a ionic species which is limitedly detected in aerosol samples. Even though the appearance of
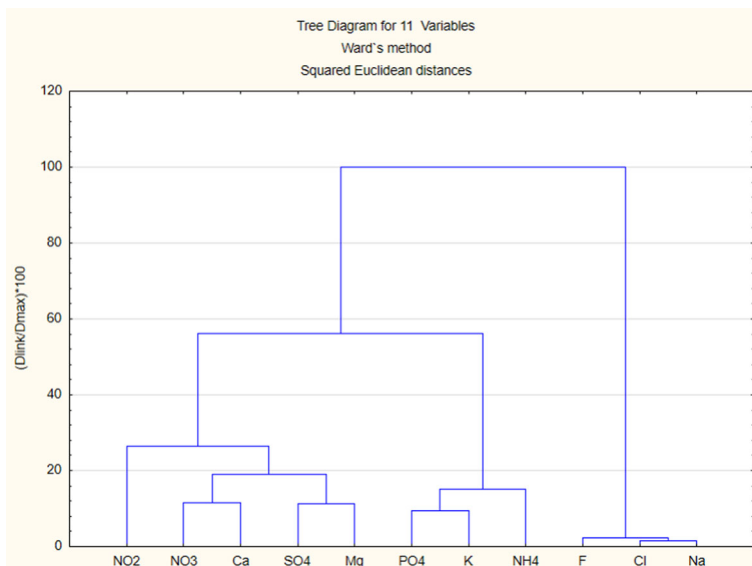

Fig. 8 Cluster analysis for Cadriano ionic composition in bulk deposition samples in the period 2009–2013, calculated with Ward's agglomerative hierarchical method and squared Euclidean distances. Similarity values are normalized to $(D_{link}/D_{max}*100)$

Table 5 Factor loadings, eigenvalues and variance resulting from the factor analysis applied on Cadriano ionic composition in 2009–2013. Loadings >0.6 are marked in bold, while loadings between 0.4 and 0.6 are in italics

	Factor 1	Factor 2	Factor 3
Na^+	0.16	**0.98**	0.04
NH_4^+	**0.83**	0.15	0.19
K^+	**0.90**	0.25	0.14
Mg^{2+}	**0.67**	0.20	*0.59*
Ca^{2+}	0.19	0.05	**0.90**
F^-	0.09	**0.97**	0.18
Cl^-	0.27	**0.93**	0.16
NO_2^-	0.11	0.26	**0.75**
NO_3^-	0.17	0.08	**0.89**
SO_4^{2-}	**0.68**	−0.03	**0.62**
PO_4^{3-}	**0.88**	0.13	0.10
Eigenvalue	6	2	1
% Total variance	51	20	14

fluorides in this factor suggests their origin from seasalt, their high EF indicates their prevailing anthropogenic origin, whose precise attribution is not possible with the sampling strategy adopted. Even though the Cadriano station is continental and not coastal, this factor explains the 20% of variance of the dataset. Therefore, we can speculate that this result could also derive from cloud processing and associated rainout over marine surfaces with inclusion of seasalt. Generally, frontal situations over marine surfaces are likely in Italy (Genoa cyclogenesis is a well-known example), but cannot be easily reconstructed, especially with a weekly sampling, which together with the collection of bulk deposition is one of the major limitations of this work.

Finally, the third factor explains the 14% of total variance and associates typical crustal markers as Ca^{2+} and Mg^{2+} with SO_4^{2-}, NO_3^-, and NO_2^-. The presence of sulphates in this factor might derive from their high correlation with Ca^{2+} and Mg^{2+}, which suggests a soil/crustal origin, linked both to Saharan dusts as well as to local soil inputs. The interpretation of the presence of nitrates and nitrites in this factor is instead not straightforward. In fact, NO_3^- is a secondary product in atmospheric aerosol typically emerging from a strong correlation with NH_4^+ which is totally absent in precipitation data herein discussed; curiously, despite the use of nitrates salts as fertilizer in the farm, nitrates only appear in Factor 3 and are therefore apparently separated from the fertilizer term including K^+, NH_4^+ and PO_4^{3-}.

Given the situation we speculate that this factor is a mixture of aerosol related species mixed to soil resuspension, the latter of which, given the experimental conditions, masks the relative contributions from other weaker sources . Multivariate analysis, though usually very efficient in solving environmental chemical fingerprints, is probably limited when carried out in such a complex environmental situation.

The analysis of significant differences of the chemical composition of bulk deposition among the three clusters of back-trajectories identified at the site indicate that they are not statistically significant different in terms of ionic composition. This confirms the finding that local resuspension is dominant over long-range transport in the collected bulk deposition samples.

While these results consequently will not allow to determine unbiased values of nitrogen fluxes, the back-trajectories analysis helped to understand the calcium origin. Ca^{2+} is generally a strong crustal indicator related to soil resuspension or to Saharan dust transports, which may reach this region either in the dry form (aeolian dust mixed to aerosol) or in the wet form,

throughout the year including winter, and with peaks in autumn. Wet-deposited dusts with a typical reddish colour are frequently observed in this region where precipitation involved may be both rainy and snowy. Some strongly impacting Saharan dust events were identified in the time series by a strong increase in Ca^{2+} and Mg^{2+}, and the analysis of back-trajectories confirmed the clear origin from the Saharan desert. An example is the event of 24–30/09/2012 (rain in Cadriano 30/09/2012), when Ca^{2+} increased until 1030 µeq l^{-1} (against an average of 516 µeq l^{-1} for the whole time series, and a 2012 yearly average equal to 545 µeq l^{-1}) and Mg^{2+} reached the concentration of 841 µeq l^{-1} (against an average of 123 µeq l^{-1} and a 2012 yearly average equal to 181 µeq l^{-1}). Figure 9 shows back-trajectories and dust load from the DREAM (Dust REgional Atmospheric Model, http://www.bsc.es/projects/earthscience/DREAM/) model for 30/09/2012, clearly confirming the impact of a Saharan dust transport affecting Cadriano during part of the sampling week and in particular during the rainy day.

4 Conclusion

This study analyses ion concentration of bulk deposition samples collected over a 5-years long period in a semi-rural area of the Po Valley, a well-known hot-spot both in terms of air quality and climate change, being a densely populated area widely exploited for intensive farming, urban and industrial settlements, frequently affected by low dispersion conditions especially during the cold season.

Chemical data were analysed using basic statistical techniques including frequency distributions and scatter plots to suitably characterize the bulk deposition. Moreover, multivariate
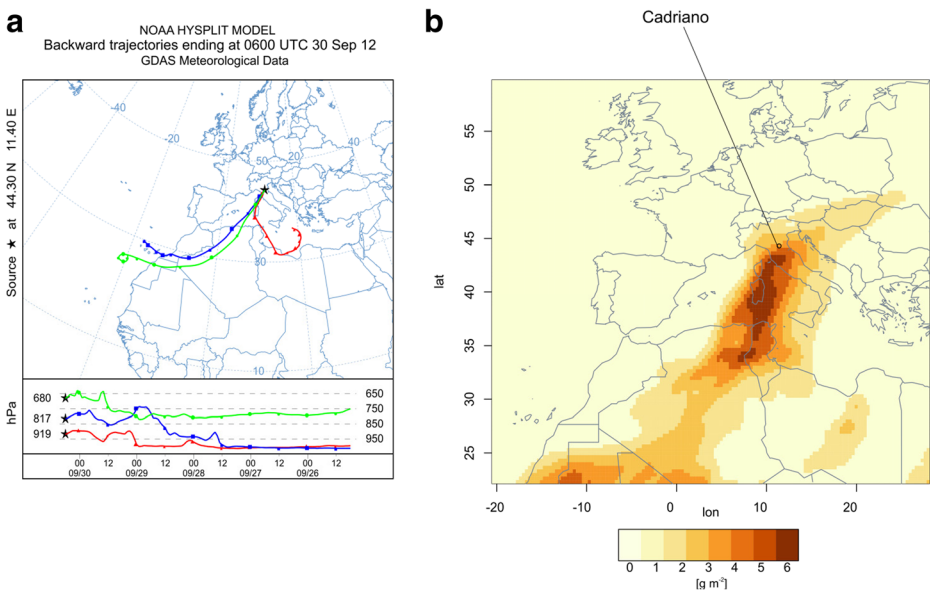

Fig. 9 a Back-trajectories (120-h backward) calculated by Hysplit-4 model using the GDAS meteorological archive, ending at Cadriano on 30th September 2012, 06 UTC and for three arrival heights: 500, 1500 and 3000 m a.s.l.; **b** Dust load simulated by the BSC-DREAM8b (Dust REgional Atmospheric Model) (http://www.bsc.es/projects/earthscience/DREAM/) dust regional model for the day 30th September 2012, 12 UTC

statistics and back-trajectories analysis were applied to identify the origin of potential emission sources affecting precipitation composition.

Results can be summarised as follows:

– bulk deposition samples were very concentrated in chemical species, both acidic and alkaline. Mean ions concentrations (in μeq l^{-1}) are the following: NO_3^- (243) > SO_4^{2-} (220) > PO_4^{3-} (176) > Cl^- (153) > NO_2^- (29) > F^- (2.6); NH_4^+ (504) > Ca^{2+} (489) > K^+ (151) > Na^+ (127) > Mg^{2+} (127).

– These ions concentrations are high compared not only to other sites located in the same district, but also worldwide. This can be explained taking into account all the possible sources such as the intense agricultural activity, industrial areas and the urban settlements. In addition, the Po Valley is characterized by a frequent stagnation of air circulation, due to the Alps and Apennines mountain chains surrounding the area on three sides.

– pH shows a tendency toward slightly alkaline condition, attributed to the large presence of ammonium and crustal elements, which mostly lead to a neutralization despite high concentrations of nitrates and sulphates.

– absence of significant differences in the chemical composition of the three clusters of back-trajectories suggests that local resuspension is dominant over long-range transport in the collected bulk deposition samples.

– The multivariate statistical analyses show that agricultural activity has a key role in the emission of NH_4^+, K^+, Ca^{2+}, and PO_4^{3-}, while Na^+ and Cl^- derive from marine salt.

– The NO_3^- origin is not straightforward. This ion is probably related to the large presence of diverse pollution sources, such as traffic, industrial settlement, agricultural activity, etc.

Even with all the limitations of the adopted sampling methodology, contributing to the not straightforward and unequivocal determination of the sources of high concentrations in ion species, our study determines important contributions deriving from the use of fertilizers and other activities such as earth moving, soil cultivation, building and road construction, to these high ion concentrations.

Even though in most countries located in the region covered by the United Nations Economic Commission for Europe (UNECE) ambient air quality has improved considerably in the last few decades, as illustrated in this study, there are areas where air quality and the concentration of chemical species in deposition still reach alarming levels, with negative impact on human health, aquatic and terrestrial ecosystems, and, last but not least, on agricultural products. In fact in an area with high density of pollution sources the agricultural sector constitutes both a cause but also a victim of pollution. Hence the importance of monitoring the most polluted areas and the elaboration of this dataset. Improving identification and knowledge of the polluting sources is needed to support further development of air policies as well as reduction strategies, as effectively done in the previous decades for acid rain.

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