Chemical and isotopic interpretation of major ion compositions from precipitation: a one-year temporal monitoring study in Wrocław, SW Poland

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Abstract The chemical compositions (Na^+ , NH_4^+ , K^+ , Mg^{2+} , Ca^{2+} , Cl^- , NO_2^- , NO_3^- , SO_4^{2-} , HCO_3^-) of wet precipitation and nitrogen isotope compositions $\delta^{15}\text{N}(\text{NH}_4^+)$ were studied from January to December 2010 in Wrocław (SW Poland). Results of a principle component analysis show that 82 % of the data variability can be explained by three main factors: 1) F1 (40 %) observed during vegetative season (electrical conductivity, HCO_3^- , NO_3^- , NO_2^- , NH_4^+ and SO_4^{2-}), mainly controlling rainwater mineralization; 2) F2 (26 %) observed during vegetative and heating seasons (K^+ , Ca^{2+} and Mg^{2+}), probably representing a combination of two processes: anthropogenic dusts and fertilizers application in agricultural fields, and 3) F3 (16 %) reported mainly during heating season (Na^+ and Cl^-) probably indicating the influence of marine aerosols. Variations of $\delta^{15}\text{N}(\text{NH}_4^+)$ from -11.5 to 18.5‰ identify three main pathways for the formation of NH_4^+ : 1) equilibrium fractionation between NH_3 and NH_4^+ ; 2) kinetic exchange between NH_3 and NH_4^+ ; 3) NH_4^+ exchange between atmospheric salts particles and precipitation. The coupled chemical/statistical analysis and $\delta^{15}\text{N}(\text{NH}_4^+)$ approach shows that while fossil fuels burning is the main source of NH_4^+ in precipitation during the heating season, during the vegetative season NH_4^+ originates from local sewage irrigation fields in *Osobowice* or agricultural fertilizers.

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1 Introduction

Precipitation is one of the best scavengers for removing particulate matter and gaseous pollutants from the atmosphere. The efficiency of this process reflects in their chemical compositions and pH values (Migliavacca et al. 2005; Prathibha et al. 2009). Chemical composition of precipitation is an important issue for many regions worldwide (e.g. Asia, eastern North America, Europe) as it can lead to eutrophication, affect ecosystems or contribute to global climate change (Calvo et al. 2010). Many studies focused on the chemical composition of rainwater from a spatio-temporal point of view (Avila 1996; Puxbaum et al. 1998; Galy-Lacaux and Modi 1998; Al-Momani et al. 2000; Topçu et al. 2002; Safai et al. 2004; Tu et al. 2005; Yoboue et al. 2005; Zhang et al. 2012) and identified several factors that can affect the chemical composition of rainwater: local pollutants, meteorological conditions, location, processes responsible for transport of pollutants (Rocha et al. 2003; Zhao et al. 2008). Chemical composition of precipitation can also provide information about both the main sources of pollutants and their migration processes (Ayres et al. 1995; Zunckel et al. 2003). A difference between ion constituents in rainwater on natural and anthropogenic sites exists. In coastal areas precipitation is mainly dominated by marine aerosols with high concentrations of Na^+ and Cl^- (Parungo et al. 1990; Ceron et al. 2002), whereas nitrogen (N) and sulphur (S) compounds dominate rural, urban and agricultural areas and reflect anthropogenic influence, such as fossil fuels combustion, fertilizers application on fields or specific sewage treatments (Das et al. 2005; Górka et al. 2014). The chemical composition of precipitation was also determined in Poland (Jóźwiak and Kozłowski 2005; Kacorzyk et al. 2012) including Wrocław and its vicinity (Kmieć et al. 1994; Czyżyk and Rajmund 2011). Chemical composition of precipitation and bulk precipitation in Wrocław is monitored by the Voivodeship Inspectorate for Environmental Protection (VIfEP) that publishes results in yearly reports (e.g. VIfEP Report 2010).

Isotope approaches as complementary tools to chemical composition of precipitation have already proven their added value to identify the origin of pollutants (e.g. Caron and Tessier 1986; Lee et al. 2012; Xiao et al. 2012; Lim et al. 2014). Similar approaches have already been used for characterising precipitation in Wrocław (SW Poland) (Górka et al. 2008; Szykiewicz et al. 2008; Górka et al. 2011). Isotopes analysis of inorganic N, an important pollutant, have also been presented by other authors (e.g. Hoering 1957; Moore 1977; Freyer 1978a, b; Heaton 1987; Xiao et al. 2012; Felix et al. 2013) however not for Poland yet to our knowledge. Atmospheric NH_3 is emitted from soils, oceans and is excreted by animals (Xiao and Liu 2002); anthropogenic sources include domestic animal excreta, fertilizers and biomass burning (Prospero et al. 1986; Hegg et al. 1988; Denterer and Crutzen 1994; Russell et al. 1998; Xiao and Liu 2002; Battye et al. 2003; Sapek 2013; Prenni et al. 2014). Nitrogen isotope composition of ammonium ($\delta^{15}\text{N}(\text{NH}_4^+)$) shows wide variations from $\delta^{15}\text{N}$ highly depleted in ^{15}N ($\sim -18.0\text{‰}$) to highly enriched in ^{15}N ($\sim 10.0\text{‰}$), depending on the origin of NH_4^+ (Moore 1977; Freyer 1978a, b; Heaton 1987). We are studying here, for the first time in Poland, the $\delta^{15}\text{N}(\text{NH}_4^+)$ in order to trace the origin of nitrogen compounds in precipitation. Principal Component Analysis (PCA) can also provide additional information about processes and

sources affecting the overall composition of precipitation (Plaisance et al. 1996; Cao et al. 2009; Calvo et al. 2010). The aim of this study is thus to characterise the processes involved in the genesis of major ions in precipitation in Wrocław. We are also investigating seasonal variability based on relationships between chemical and isotope characteristics. This study uses a novel approach for characterising precipitation using an approach coupling chemical, isotope and statistical data from a 1-year (2010) monitoring in Wrocław.

2 Materials and methods

2.1 Study area

Wrocław is the largest city (630,000 inhabitants) in the Lower Silesia region in southwestern Poland, at the feet of the Sudety Mountains. Surface area of the city is 293 km², and consists of: agricultural lands (132 km²), forests and woodlands (16.5 km²), water (9.6 km²), wasteland (3.9 km²), roads (28.48 km²), habitations (85.08 km²), the irrigation fields of *Osobowice* (11 km²) and others (17.44 km²). On its western part Wrocław is surrounded by agricultural lands. 5 large rivers flow through the city: the Odra River and its 4 tributaries (Oława, Widawa, Bystrzyca, Ślęza). 3 trans-national roads run through Wrocław. There are also two large railway stations, two inland navigation ports and one international airport. Wrocław is influenced by a temperate climate characterized by both continental and marine contexts. Wind directions are mainly western (27.6 % days) and southern (23.1 %) with an average speed around 2.5 m·s⁻¹. The mean annual temperature is 9.6 °C and the yearly rainfall average is 589 mm (Dubicki et al. 2002).

2.2 Samples collection

Rain samples were collected using a rain collector located in downtown Wrocław (Poland) (Fig. 1).

Forty-one precipitation samples (wet deposition) were collected at a 2 m height from January 2010 to December 2010 via a funnel (diameter of 0.8 m) into 5 L plastic containers covered by plastic a grid to prevent contamination. The funnel was placed in an open space to avoid any canopy effect.

2.3 Chemical analysis

Each sample was filtered through a 1.2 µm GF/C filter to remove organic pollution. Electrical conductivity (EC) was measured using a Multi 340i WTW multiparameter gauge with a TetraCon 325/S electrode (precision of ±1 %). pH of rainfall was calculated from the equation: $\text{pH} = 6.37 + \log \text{Alk} (\text{meq.L}^{-1})$ (Gomółka 1998). For alkalinity samples were titrated with 0.1 M HCl (methyl orange used as a pH indicator) using automatic pipette (OP200 HTL; precision of 20 µL) for estimating the presence of carbonic acid. Cations (Na^+ , NH_4^+ , K^+ , Mg^{2+} , Ca^{2+}) and anions (Cl^- , NO_2^- , NO_3^- , SO_4^{2-}) were measured using Alliance Waters High-Performance Liquid Chromatograph (HPLC) 2695 with a 432 Conductivity Detector and a 2998 Photodiode Array Detector, an IC-Pak Anion HR column (glauconate/borate eluent) and IC-Pak Cation M/D column (EDTA/HNO₃ eluent). Before measurements each sample was filtered

Fig. 1 Location of sampling area (Wrocław, SW Poland)

through a 0.2 μm syringe filter. The analytical precision of measurement for these ions was $0.01 \text{ mg} \cdot \text{L}^{-1}$. Using a 100- μL injection, the estimated method's detection limits (MDLs) were, in ppb: Cl^- (50), NO_2^- (50), NO_3^- (75), SO_4^{2-} (75), K^+ (15), Na^+ (5), Mg^{2+} (10), NH_4^+ (5), Ca^{2+} (15).

Ion were preconcentrated using ion exchange resins. Before gravity dripping through resins, samples were filtered through the GF/C filter and then placed in a 1 L glass separatory funnel. Bio-Rad AG 50W-X8 (hydrogen form) resin was used for the analysis due to its relatively high affinity for NH_4^+ (Silva et al. 2000). Prior to dripping ions from the resin, the reagents as well as quartz wool and quartz tubes were prepared according to following steps:

1. CuO and Cu were calcinated at 400 $^\circ\text{C}$ for about 4 h in a muffle furnace to clean the reagents.
2. The CaO fraction of 1–2 mm was prepared following the procedures described in Boyd et al. (1994) and Kendall and Grim (1990).
3. Quartz tube (20 cm length and 9 mm diameter) and quartz wool were calcinated at 900 $^\circ\text{C}$ for about 1 h.

2.4 Procedure for eluting NH_4^+ ions from the cation exchange resin column and analysing its $\delta^{15}\text{N}$

Following the procedure described in Lehmann et al. (2001), the cation exchange resin loaded with NH_4^+ was dried in a muffle furnace at 50 $^\circ\text{C}$ and homogenized using an agate mortar. It

was then loaded in a cleaned quartz tube with combustion reagents in the following order: (i) ground resin containing the NH_4^+ ions, (ii) 100 mg of copper oxide (CuO), (iii) 200 mg of copper (Cu), (iv) 500 mg of calcium oxide (CaO), 100 mg of CuO , (v) 200 mg of Cu and (vi) 500 mg of CaO . The tube was pumped down to 10^{-3} mbar and sealed hermetically and burnt for 10 h in a muffle furnace following the modified procedure of Kendall and Grim (1990): (i) raising the temperature up to 900 °C within 1 h (ii) maintaining the temperature at 900 °C for 4 h, (iii) cooling down to 600 °C for 3 h and (iv) maintaining for 2 h at 600 °C and finally cooling down to room temperature. At 900 °C, organic pollutants are burnt and AgNO_3 reacts with oxygen liberated by the CuO . At 600 °C the carbon dioxide generated by the combustion of organic pollutants reacts with CaO to form calcium carbonate. At room temperature, created water is adsorbed onto the CaO particles to form Ca(OH)_2 . During the cooling steps nitrogen oxides are also reduced to N_2 by Cu , which does not require additional cryogenic purification and is ultimately used to measure the isotope ratio $^{15}\text{N}/^{14}\text{N}$ (Kendall and Grim 1990).

Analysis of the N isotope composition was carried out on a dual inlet Delta V Advantage mass spectrometer in the Laboratory of Isotope Geology and Geoecology at the Institute of Geological Sciences, University of Wrocław. International standards IAEA N-1 and N-2 were used to calibrate the data. $\delta^{15}\text{N}$ are reported relative to atmospheric nitrogen (N_2 -Air). The error of the $\delta^{15}\text{N}$ determination is below 0.5‰.

2.5 Statistical analysis

Principal Component Analysis (PCA) is a very proven statistical method to characterise the spatio-temporal variability of large data population (e.g. Zhang et al. 1992; Manly 1998, Eder et al. 2014). PCA allows to abstract factors describing the variability of analysed population by using correlation matrixes and were used here with the intent to: (i) analyse the variability of several precipitation events simultaneously, (ii) discriminate sources of ions in precipitation, (iii) determine the respective contributions of those sources. PCA was carried out for 11 parameters: electrical conductivity (EC), HCO_3^- , Cl^- , NO_2^- , NO_3^- , SO_4^{2-} , Na^+ , NH_4^+ , K^+ , Mg^{2+} and Ca^{2+} . PCA followed several steps: (i) elimination, (ii) testing of the distribution normality, (iii) choosing parameters for analysis, (iv) standardisation, (v) parameters transformation using the PCA method, (vi) “varimax” rotation, (vii) factor’s loading and factor’s scores extraction and interpretation of its variability (Johnson 1978; Manly 1998).

3 Results

3.1 Weather conditions

Air temperature varied from −11 °C (December 4, 2010) to 26 °C (July 13, 2010) with an average value of 10.6 °C (median: 10 °C) (Table 1; Supplementary Materials). The average annual temperature (8.4 °C) for 2010 was about 1.2 °C lower than the 9-year average measured between 2000 and 2009 (Dubicki et al. 2002). We divided the calendar year into three distinct periods according to the meteorological data: vegetative season and 2 heating seasons. Vegetative season is defined as the period where the daily average temperature is higher than 5 °C. For 2010 we thus adopted the following periods: heating season I (January 14 to April 04), vegetative season (April 9 to October 16) and heating season II (October 13 to December 25).

The sum of yearly precipitation (751 mm) (Meteorological Bulletin 2010) was significantly higher than average value observed from 2000 to 2009 (589 mm) (Dubicki et al. 2002).

The calculated pH in precipitation ranged from 4.5 (December 25, 2010) to 5.8 (May 3, 2010), with a mean value of 5.2 (median: 5.2) (Table 1; Supplementary Materials) and correspond to the ranges determined by VIEP in Wrocław (VIEP Report 2010). EC in precipitation varied from 12 (December 25, 2010) to 162 $\mu\text{S}\cdot\text{cm}^{-1}$ (March 13, 2010), with a mean value of 71 $\mu\text{S}\cdot\text{cm}^{-1}$ (median: 61 $\mu\text{S}\cdot\text{cm}^{-1}$) (Table 1; Supplementary Materials).

3.2 Chemical composition of precipitation

NO_2^- concentrations varied from $<0.01 \text{ mg}\cdot\text{L}^{-1}$ (May 21, 31, November 14, and December 12, 25, 2010) to $2.9 \text{ mg}\cdot\text{L}^{-1}$ (April 26, 2010) with an average value $0.9 \text{ mg}\cdot\text{L}^{-1}$ (median: $0.7 \text{ mg}\cdot\text{L}^{-1}$), NO_3^- ranged from $<0.01 \text{ mg}\cdot\text{L}^{-1}$ (May 21 and November 14, 2010) to $16.5 \text{ mg}\cdot\text{L}^{-1}$ (April 26, 2010) with an average value of $4.6 \text{ mg}\cdot\text{L}^{-1}$ (median: $3.71 \text{ mg}\cdot\text{L}^{-1}$), whereas NH_4^+ concentrations ranged from $<0.01 \text{ mg}\cdot\text{L}^{-1}$ (May 19, 21 and December 4, 2010) to $7.9 \text{ mg}\cdot\text{L}^{-1}$ (April 26, 2010) with an average value of $2.8 \text{ mg}\cdot\text{L}^{-1}$ (median: $2.1 \text{ mg}\cdot\text{L}^{-1}$) (Table 1).

Ca^{2+} varied from $0.1 \text{ mg}\cdot\text{L}^{-1}$ (December 25, 2010) to $6.9 \text{ mg}\cdot\text{L}^{-1}$ (July 13, 2010) with a mean value of $2.2 \text{ mg}\cdot\text{L}^{-1}$ (median: $1.5 \text{ mg}\cdot\text{L}^{-1}$), Mg^{2+} from $0.05 \text{ mg}\cdot\text{L}^{-1}$ (December 25, 2010) to $1.0 \text{ mg}\cdot\text{L}^{-1}$ (December 5, 2010) with a mean value of $0.3 \text{ mg}\cdot\text{L}^{-1}$ (median: $0.2 \text{ mg}\cdot\text{L}^{-1}$), K^+ from $<0.01 \text{ mg}\cdot\text{L}^{-1}$ (December 5, 25, 2010) to $23.0 \text{ mg}\cdot\text{L}^{-1}$ (November 14, 2010) with a mean value $2.9 \text{ mg}\cdot\text{L}^{-1}$ (median: $1.6 \text{ mg}\cdot\text{L}^{-1}$), Na^+ from $<0.01 \text{ mg}\cdot\text{L}^{-1}$ (April 5, August 31, October 13, 2010) to $12.9 \text{ mg}\cdot\text{L}^{-1}$ (December 5, 2010) with a mean value of $2.4 \text{ mg}\cdot\text{L}^{-1}$ (median: $1.7 \text{ mg}\cdot\text{L}^{-1}$), SO_4^{2-} from $<0.01 \text{ mg}\cdot\text{L}^{-1}$ (April 11, November 22, December 25, 2010) to $24.5 \text{ mg}\cdot\text{L}^{-1}$ (November 10, 2010) with a mean value of $8.1 \text{ mg}\cdot\text{L}^{-1}$ (median: $5.6 \text{ mg}\cdot\text{L}^{-1}$), Cl^- from $0.7 \text{ mg}\cdot\text{L}^{-1}$ (May 19, 2010) to $18.6 \text{ mg}\cdot\text{L}^{-1}$ (November

Table 1 Descriptive statistics for the main parameters

	Parameter	Unit	N	Mean	Median	Minimum	Maximum	Standard deviation
Precipitation	EC	$\mu\text{S}\cdot\text{cm}^{-1}$	41	71	61	12	162	36
	pH	–	41	5.20	5.20	4.45	5.82	0.56
	HCO_3^-	$\text{mg}\cdot\text{dm}^{-3}$	41	5.73	4.15	0.73	17.09	4.39
	Cl^-	$\text{mg}\cdot\text{dm}^{-3}$	41	4.06	2.75	0.70	18.63	3.86
	NO_2^-	$\text{mg}\cdot\text{dm}^{-3}$	41	0.96	0.67	<0.01	2.93	0.78
	NO_3^-	$\text{mg}\cdot\text{dm}^{-3}$	41	4.52	3.71	<0.01	16.49	3.50
	SO_4^{2-}	$\text{mg}\cdot\text{dm}^{-3}$	41	8.12	5.62	<0.01	24.51	5.79
	Na^+	$\text{mg}\cdot\text{dm}^{-3}$	41	2.36	1.73	<0.01	12.86	2.49
	NH_4^+	$\text{mg}\cdot\text{dm}^{-3}$	41	2.46	2.12	<0.01	7.92	1.75
	K^+	$\text{mg}\cdot\text{dm}^{-3}$	41	2.85	1.62	0.01	22.95	4.18
	Mg^{2+}	$\text{mg}\cdot\text{dm}^{-3}$	41	0.25	0.17	0.05	0.97	0.18
	Ca^{2+}	$\text{mg}\cdot\text{dm}^{-3}$	41	2.15	1.50	0.14	6.93	1.70
	$\delta^{15}\text{N}_{\text{N}_2\text{-Air}}(\text{NH}_4^+)$	‰	29*	2.1	1.3	–11.5	18.5	6.8
Air	Air temperature	$^{\circ}\text{C}$	41	10.6	10.0	–11.0	26.0	8.4

* For the isotope analysis we only considered rainwater samples whose volume was greater than 1 l or generated a sufficient ionization current that allowed a proper analysis. In total we analysed 29 samples out of 41 collected

10, 2010) with a mean value of $4.1 \text{ mg}\cdot\text{L}^{-1}$ (median: $2.8 \text{ mg}\cdot\text{L}^{-1}$) and HCO_3^- from $0.7 \text{ mg}\cdot\text{L}^{-1}$ (December 25, 2010) to $17.1 \text{ mg}\cdot\text{L}^{-1}$ (March 3, 2010) with a mean value of $5.7 \text{ mg}\cdot\text{L}^{-1}$ (median: $4.2 \text{ mg}\cdot\text{L}^{-1}$) (Table 1).

3.3 Nitrogen isotope composition ($\delta^{15}\text{N}$) of NH_4^+

$\delta^{15}\text{N}$ of NH_4^+ showed large fluctuations during the study period from -11.5 (January 28) to $+18.5\%$ (August 31) with an average value of 2.1% (median: 1.3%) (Table 1).

4 Discussion

4.1 Sources and process controlling the chemical composition of rainwater

The chemical compositions of precipitation showed during 2010 a significant variability with time (Figs. 2 and 3) that may indicate that either one or different processes are involved or/and that this/these process(es) vary(ies) with time. PCA can help alleviate this difficulty by distinguishing processes that control the chemical composition of rainwater (Zhang et al. 1992) as well as help estimate the intensity of these processes by the study of factor scores. Extreme negative values (<-1) indicate that the specific processes that each factor represents do not affect samples. In contrast, positive values ($>+1$) indicate they are strongly impacted by these processes. Values between -1 and $+1$ define the “mixing zone” of individual processes (Manly 1998; Jolliffe 2002).

PCA, in our case, explains 82 % of the observed chemical variations (Table 2). The remaining 18 % were considered as “random noise” that can not be interpreted using this technique (Drever 1997; Manly 1998). Results suggest that chemical and isotope compositions of our precipitation are formed/controlled by at least three distinct factors (Table 2) interpreted as natural and anthropogenic processes or a mixing of both.

4.1.1 Factor 1

Factor 1 accounted for nearly 40 % of the total variance, had high positive factors for EC, HCO_3^- , NO_3^- , NO_2^- , NH_4^+ and SO_4^{2-} (Table 2) probably hinting that they may have a common origin. Strong correlation between mineral forms of nitrogen and sulphate ions is observed in many rainwater studies worldwide (e.g. Plaisance et al. 1997; Cao et al. 2009; Calvo et al. 2010) and usually is interpreted by the authors as a mixing of emissions from different anthropogenic sources.

NO_2^- and NO_3^- yielded maximum concentrations in spring at the beginning of vegetative season (Figs. 2 and 3) with values of $2.9 \text{ mg}\cdot\text{L}^{-1}$ and $16.5 \text{ mg}\cdot\text{L}^{-1}$, respectively (Table 1; Supplementary Materials; Fig. 2). These concentrations are unexpectedly higher than those reported for the Lower Silesia Region and rural areas in other countries (Cao et al. 2009; Wang and Han 2011). For 2010, the Voivodeship Inspectorate for Environmental Protection for whole voivodeship (VIeEP Report 2010) reports combined ($\text{NO}_2^- + \text{NO}_3^-$) concentrations from $0.02 \text{ mg}\cdot\text{L}^{-1}$ to $3.6 \text{ mg}\cdot\text{L}^{-1}$, still lower than our data obtained in Wrocław. Annual averages of NO_3^- concentrations in the Sudety Mountains (SW Poland) ranged from 1.9 to $2.7 \text{ mg}\cdot\text{L}^{-1}$ between 1988 and 1992 (Kmieć et al. 1994) and from 0.6 to $1.5 \text{ mg}\cdot\text{L}^{-1}$ in the vicinity of Wrocław between 2002 and 2010 (Czyżyk and Rajmund 2011). Our NH_4^+ concentrations in

Fig. 2 Temporal variability of concentration of anions in precipitation water sampled in Wrocław in 2010

precipitation ranged from $<0.01 \text{ mg} \cdot \text{L}^{-1}$ to $7.9 \text{ mg} \cdot \text{L}^{-1}$ in 2010. Kmiec et al. (1994) reported for 1994 NH_4^+ values from 2.3 to $3.9 \text{ mg} \cdot \text{L}^{-1}$ similar to the highest values we observed during the vegetative season (Fig. 4). Those spring maximum concentrations of N mineral forms may be related to the plants biological activity caused by the application of fertilizer onto

Fig. 3 Temporal variability of concentration of cations in precipitation water sampled in Wrocław in 2010

agricultural fields during spring (Freyer 1978a, b). The concomitant NH_4^+ peak may be related to an increase in the rate of NH_4^+ volatilization from agricultural fields (fertilized with manure and/or urea). NH_4^+ volatilization results from the temperature-controlled bacterial enzymatic

Table 2 Results of the Principal Component Analysis (PCA) for precipitation water collected in Wrocław in 2010

Parameter	Factor 1	Factor 2	Factor 3
EC [$\mu\text{S}\cdot\text{cm}^{-1}$]	0.71	0.50	0.48
HCO_3^- [$\text{mg}\cdot\text{L}^{-1}$]	0.78	−0.11	−0.02
Cl^- [$\text{mg}\cdot\text{L}^{-1}$]	0.36	0.47	0.66
NO_2^- [$\text{mg}\cdot\text{L}^{-1}$]	0.87	−0.08	0.03
NO_3^- [$\text{mg}\cdot\text{L}^{-1}$]	0.89	0.07	0.07
SO_4^{2-} [$\text{mg}\cdot\text{L}^{-1}$]	0.78	0.13	0.53
Na^+ [$\text{mg}\cdot\text{L}^{-1}$]	−0.11	−0.00	0.86
NH_4^+ [$\text{mg}\cdot\text{L}^{-1}$]	0.75	0.13	−0.26
K^+ [$\text{mg}\cdot\text{L}^{-1}$]	−0.26	0.90	0.03
Mg^{2+} [$\text{mg}\cdot\text{L}^{-1}$]	0.07	0.96	0.12
Ca^{2+} [$\text{mg}\cdot\text{L}^{-1}$]	0.56	0.76	0.05
Factor contribution [%]	40	26	16

Bold text indicates values considered as significant (−0.6/+0.6)

activity, where the urease enzyme catalyses the release of NH_4^+ from urea (Torello and Wehner 1983). Therefore an increase in the NH_4^+ volatilisation rate is expected during spring especially when considering other local conditions: predominance of sandy soils with expected low cations exchange capacities, high soil moisture, periodical flooding, crop residues (Ernst and Massey 1960; Torello and Wehner 1983; Tomassi-Morawiec et al. 1998).

SO_4^{2-} concentrations, from $<0.01 \text{ mg}\cdot\text{L}^{-1}$ to $24.5 \text{ mg}\cdot\text{L}^{-1}$, were higher during heating periods (related to fossil fuels combustion) than during the vegetative season. An elevated spring concentration pick was also observed (Fig. 2). Similarly to NO_2^- and NO_3^{2-} SO_4^{2-} concentrations were higher in Wrocław than in the whole voivodeship (0.3 to $15.1 \text{ mg}\cdot\text{L}^{-1}$; VIeP Report 2010). In the near Sudety Mountains SO_4^{2-} concentrations in precipitation range from 9.1 to $15.4 \text{ mg}\cdot\text{L}^{-1}$ (Kmieć et al. 1994) and from 3.1 to $9.4 \text{ mg}\cdot\text{L}^{-1}$ in the vicinity of Wrocław (Czyżyk and Rajmund 2011). Additionally, during the heating season II two higher concentrations of NO_3^- and NO_2^- (coupled to high SO_4^{2-} episodes) were observed (Fig. 1). Analysis of the variability of NO_3^- , NO_2^- , NH_4^+ , SO_4^{2-} ions and PCA correlation shows that in Wrocław they likely result from a mixing of two or three main anthropogenic sources: 1) application of fertilizers, 2) combustion of fossil fuels and 3) emissions from local *Osobowice* sewage irrigation fields. Though processes have not been fully characterised, SO_4^{2-} , NO_3^- and NH_4^+ can also be produced as secondary inorganic aerosols (SIA) through photochemical reactions between gaseous pollutants and primary aerosols (Baker and Scheff 2007; Behera and Sharma 2011). Still, multiple atmospheric reactions may explain the strong correlation existing between these ions and ultimately play a role in the formation of the chemical composition of precipitation in Wrocław. Analysis of factor 1 scores shows that highest values (>1) are observed during the vegetative season (spring maximum; Fig. 4), indicating that these processes are dominant during this period. During the rest of the year they are contributing less (“mixing zone” in Fig. 4). Processes represented by factor 1 largely determine the rainwater mineralization as evidenced by its strong correlation with both EC and HCO_3^- concentrations.

Fig. 4 Temporal variability of factor scores calculated via PCA for precipitation water sampled in Wrocław in 2010

4.1.2 Factor 2

Factor 2 accounted for 26 % of the total variance and had high positive factor loadings for K^+ , Ca^{2+} and Mg^{2+} . The fact that the PCA identifies these components as a factor suggests that their main sources in precipitation are probably distinct than those for NO_3^- , NO_2^- , NH_4^+ and SO_4^{2-} . Ca^{2+} concentrations, obtained in this study, ranged from $0.1 \text{ mg}\cdot\text{L}^{-1}$ to $6.9 \text{ mg}\cdot\text{L}^{-1}$ consistent with concentrations reported by VifEP ($0.1\text{--}7.1 \text{ mg}\cdot\text{L}^{-1}$), Kmiec et al. (1994; 2.0 to $2.7 \text{ mg}\cdot\text{L}^{-1}$) and Czyżyk and Rajmund (2011; 0.5 to $2.5 \text{ mg}\cdot\text{L}^{-1}$). VifEP reports slightly higher Mg^{2+} concentrations ($0.1\text{--}1.6 \text{ mg}\cdot\text{L}^{-1}$) than those measured in this study ($0.1\text{--}1.0 \text{ mg}\cdot\text{L}^{-1}$). Previous studies (1988–1992 and 2002–2010) yielded lower concentration ranges for Mg^{2+} , from 0.3 to $0.5 \text{ mg}\cdot\text{L}^{-1}$ and from 0.1 to $0.4 \text{ mg}\cdot\text{L}^{-1}$, respectively (Kmiec et al. 1994 and Czyżyk and Rajmund 2011). K^+ concentrations as high as $22.9 \text{ mg}\cdot\text{L}^{-1}$ significantly higher

than those measured by VifEP ($0.1\text{--}2.9\text{ mg}\cdot\text{L}^{-1}$) as well as in previous studies: $1.1\text{ to }3.8\text{ mg}\cdot\text{L}^{-1}$ (Kmieć et al. 1994) and $0.5\text{ to }2.7\text{ mg}\cdot\text{L}^{-1}$ (Czyżyk and Rajmund 2011).

For K^+ , Ca^{2+} and Mg^{2+} (Fig. 3) and factor 2 scores (Fig. 4) the highest values were observed 2–3 times during the vegetative season and once during the heating season II. The rest of the year, values plotted in the “mixing zone” (Fig. 4). These ions can have either a crustal (Ca^{2+} , Mg^{2+} , K^+ are present in weathering products minerals) or anthropogenic origin (e.g. vehicle roadside dust, industrial aerosol) (Plaisance et al. 1997; Ali et al. 2004; Cao et al. 2009; Wang and Han 2011). Once emitted in the atmosphere they can be flushed following interaction with rainwater. But we observed no significant correlation between the volume of precipitation and these ions concentrations except once during the heating season II. Low precipitation can also lead to an increase in their corresponding concentrations. K^+ , Mg^{2+} and Ca^{2+} are ubiquitous in fertilizers, including ammonium nitrate (NH_4NO_3) and ammonium sulphate ($(\text{NH}_4)_2\text{SO}_4$), which probably represent one of these ions sources in factor 1. In particular the fact that potassium fertilizers, such as KCl and K_2SO_4 , are often applied or re-applied in autumn and winter season in Europe (Crous et al. 2008; Hejzman et al. 2012; Shield et al. 2014) may explain the K^+ peak observed in autumn (Fig. 2). Potassium ions also tend to accumulate in top layers in fertilized soils, which can facilitate their transfer to the atmosphere during soil dust suspension (Shield et al. 2014). This suggests that factor 2 may represent a mixing of two processes: 1) natural and anthropogenic dusts emissions and 2) application of fertilizers (containing K^+ , Ca^{2+} and Mg^{2+}) to tillage soils. The absence of correlation between components from PCA factors 1 and 2 also favours volatilisation during application of fertilizers, irrigation fields activity as the main source of NH_4^+ as further field tilling is expected to generate dust, the main component of factor 2.

4.1.3 Factor 3

Factor 3 accounted for 16 % of the total variance and yielded high positive factor values for Na^+ and Cl^- , that probably represent marine aerosols and dry deposition (Plaisance et al. 1997; Błaś et al. 2010; Calvo et al. 2010). Na^+ concentration ranged from $<0.01\text{ to }12.9\text{ mg}\cdot\text{L}^{-1}$ and Cl^- from $0.7\text{ mg}\cdot\text{L}^{-1}$ to $18.6\text{ mg}\cdot\text{L}^{-1}$, higher than the values measured by VifEP in Wrocław and the whole voivodeship (Na^+ from $0.01\text{ to }2.6\text{ mg}\cdot\text{L}^{-1}$ and Cl^- from $0.05\text{ to }6.5\text{ mg}\cdot\text{L}^{-1}$) and from previous studies: Na^+ from $1.5\text{ to }1.9\text{ mg}\cdot\text{L}^{-1}$, Cl^- from $3.8\text{ to }5.0\text{ mg}\cdot\text{L}^{-1}$ (Kmieć et al. 1994) and Na^+ from $0.9\text{ to }3.2\text{ mg}\cdot\text{L}^{-1}$, Cl^- from $3.1\text{ to }5.7\text{ mg}\cdot\text{L}^{-1}$ (Czyżyk and Rajmund 2011). The median value for the Cl/Na ratio in precipitation was above 1.17, the typical for seawater, but along the year extremely high (367) and low (0.15) Cl/Na ratios were also observed. Analysis of the variability of Na^+ , Cl^- and factor 3 values suggest that the processes represented by factor 3 affected the composition of precipitation throughout the year but dominated during the winter periods.

4.2 Origin of NH_4^+ concentrations and $\delta^{15}\text{N}(\text{NH}_4^+)$ isotope compositions

The NH_4^+ concentrations ranged from $<0.01\text{ to }7.9\text{ mg}\cdot\text{L}^{-1}$ with an average value of $2.5\pm 1.8\text{ mg}\cdot\text{L}^{-1}$ and $\delta^{15}\text{N}(\text{NH}_4^+)$ values ranged from $-11.5\text{ to }18.5\text{‰}$ with an average value of $2.1\pm 6.8\text{‰}$, which both represent wider ranges than those obtained by other authors (Fig. 6) (Hoering 1957; Moore 1974; Freyer 1978a, b; Heaton 1987; Paerl and Fogel 1994; Gao 2002). This large fluctuation of $\delta^{15}\text{N}(\text{NH}_4^+)$ may indicate that several sources of nitrogen compounds are involved or that secondary processes are significantly fractionating initial isotope compositions.

Temporal variations of NH_4^+ concentrations in precipitation clearly identify two distinct periods corresponding to two peaks in NH_4^+ concentrations (Fig. 5): (i) early spring, and (ii) early autumn. In both cases the maximum NH_4^+ concentration is probably due to (i) increased application of fertilizers in local agricultural fields 1) at the beginning of the vegetation period and then in autumn for autumn-sown cereal or 2) biological activity at the local *Osobowice* sewage irrigation fields. The variations in NH_4^+ concentrations do not seem to correlate with the corresponding $\delta^{15}\text{N}(\text{NH}_4^+)$ as we are observing a rough ^{15}N enrichment along the whole season (Fig. 5).

The lack of simple correlation of NH_4^+ concentrations ($1/\text{NH}_4^+$ ratio) with the corresponding $\delta^{15}\text{N}(\text{NH}_4^+)$ were confirmed by statistical tests ($R=-0.07$ and $R=-0.08$, respectively, $p<0.05$). This is probably caused by a complex atmospheric open system controlled by numerous intricate nitrogen sources, conditions (e.g. temperature, pressure) and secondary processes that may fractionate nitrogen isotopes. However, our data show positive relations between the daily average temperature and $\delta^{15}\text{N}(\text{NH}_4^+)$, and daily average temperature and NH_4^+ concentrations (Fig. 5), confirmed by significant statistical correlations ($R=0.38$ and $R=0.70$ respectively; $p<0.05$). Figure 6 reports variations of NH_4^+ concentrations and $\delta^{15}\text{N}(\text{NH}_4^+)$ for each identified 3 seasons (heating I, vegetation and heating II). Results indicate that all data can be explained by at least the three following end-members (two at low NH_4^+ concentrations and one dominant at NH_4^+ concentrations higher than $8 \text{ mg} \cdot \text{L}^{-1}$): 1) Low NH_4^+ and high $\delta^{15}\text{N}$ ($>20\text{‰}$), 2) low NH_4^+ and low $\delta^{15}\text{N}$ ($<15\text{‰}$) and 3) high NH_4^+ ($>8 \text{ mg} \cdot \text{L}^{-1}$) and a $\delta^{15}\text{N}$ around 0‰ .

Fig. 5 $\delta^{15}\text{N}_{\text{N}_2\text{-Air}}(\text{NH}_4^+)$, NH_4^+ concentration in precipitation and air temperature during sampling period. Air temperature values from www.wunderground.com

Fig. 6 Relationship between ammonium concentration and $\delta^{15}\text{N}_{\text{N}_2\text{-Air}}(\text{NH}_4^+)$ in precipitation. Values of ammonium concentration and $\delta^{15}\text{N}_{\text{N}_2\text{-Air}}(\text{NH}_4^+)$ values are from: Hoering 1957; Moore 1974; Freyer 1978a, b; Heaton 1987; Paerl and Fogel 1994 and Gao 2002

Three main processes may control the final $\delta^{15}\text{N}(\text{NH}_4^+)$ in this study (Fig. 7): 1) PROCESS 1: equilibrium fractionation between NH_3 and NH_4^+ ; 2) PROCESS 2: kinetic exchange reactions between NH_3 and NH_4^+ ; and 3) PROCESS 3: exchange reactions between atmospheric NH_4^+ in salt aerosols and NH_4^+ in precipitation. Variations of air temperature with $\delta^{15}\text{N}(\text{NH}_4^+)$ in precipitation (Fig. 7a) discriminate samples into two distinct groups depending on the season: (I) vegetative and (II) heating seasons.

If we assume an equilibrium isotope fractionation between NH_3 and NH_4^+ in precipitation we can try to estimate the $\delta^{15}\text{N}$ of NH_3 from which NH_4^+ was formed. Volatilization of urea (e.g. manure) in soils follows a Rayleigh distillation that is highly favouring ^{15}N , resulting in $\Delta^{15}\text{N}$ in volatilized NH_3 around 35‰ (Frank et al. 2004) and even 30–60‰ (Högberg 1997; Robinson 2001). Similarly, the process of volatilizing fertilizers (with $\delta^{15}\text{N}$ around 0.2‰; Bateman and Kelly 2007) produces NH_3 with $\delta^{15}\text{N}$ between -48.0 and -36.3‰, which represents a similar nitrogen isotope fractionation (Δ) as for urea. However, isotopically describing the opposite process of dissolving NH_3 in atmospheric water into NH_4^+ is probably more complicated. Still, we can estimate the $\delta^{15}\text{N}$ of potential sources atmospheric NH_3

Fig. 7 Possible explanations of precipitation ammonium origin basing of $\delta^{15}\text{N}(\text{NH}_4^+)$. **a** Fractionation equation from Scalán 1958. **b** Vehicle exhaust, cow waste, volatilized fertilizer levels from Felix et al. 2013 and brown and hard coal level from Freyer 1978a, b. **c** Possible kinetic exchange reactions from Freyer 1978a, b and Heaton 1987; $\delta^{15}\text{N}(\text{NH}_4^+)$ levels for tropospheric aerosols from Moore 1977, fertilizer from Shearer et al. 1974 and for soil NH_4^+ from Freyer 1978a, b. Process 1 - Measured $\delta^{15}\text{N}(\text{NH}_4^+)$ values were converted to theoretical $\delta^{15}\text{N}(\text{NH}_3)$ assuming equilibrium exchange; Process 2 - Measured $\delta^{15}\text{N}(\text{NH}_4^+)$ values were converted to theoretical $\delta^{15}\text{N}(\text{NH}_3)$ assuming kinetic exchange; Process 3 - Measured $\delta^{15}\text{N}(\text{NH}_4^+)$ values were converted to theoretical $\delta^{15}\text{N}(\text{NH}_4^+)$ assuming atmospheric solid NH_4^+ exchange

sources from the values of $\delta^{15}\text{N}(\text{NH}_4^+)$ values and daily air temperature using the $\text{NH}_4^+ - \text{NH}_3$ equation described in Scalan et al. (1958) and in Busigny and Bebout (2013). Results give a range of $\delta^{15}\text{N}(\text{NH}_3)$ from -35.0 to -13.2‰ sample group I during vegetative season (Fig. 7b) that implies involving two main sources of NH_3 : 1) animal waste with $\delta^{15}\text{N}(\text{NH}_3)$ values from -28.5 to -22.8‰ , (Felix et al. 2013) and fertilizers with $\delta^{15}\text{N}(\text{NH}_3)$ values from -48.0 to -36.3‰ , (Felix et al. 2013). While our isotope data do not contradict fertilisers or sewage irrigation fields as the main sources of atmospheric NH_3 in Wrocław during the vegetative season, it does not unambiguously comfort this hypothesis as NH_3 volatilisation from fertilizer, manure, urea produces overlapping $\delta^{15}\text{N}(\text{NH}_3)$ ranges. If PROCESS 1 is actually controlling the atmospheric budget of NH_3 in the atmosphere of Wrocław it would imply that during the vegetative season fertilisers and manure are the dominant sources of NH_3 , compared to vehicle and industrial emissions. For samples in group II that correspond to heating seasons I & II (Fig. 7a) we cannot use the Scalan equation as it is not suited for temperatures below 0°C . At these temperatures a nitrogen exchange between $\text{NH}_3 - \text{NH}_4^+$ in a solid matrix (snow) is rather impossible. Kinetic exchange reactions between NH_3 and NH_4^+ in rainwater (PROCESS 2) is another possibility for explaining $\delta^{15}\text{N}(\text{NH}_4^+)$ of samples from group II (Fig. 7a). The induced nitrogen isotope effect is still subject to debate as some studies report that NH_4^+ ions in rainwater are slightly depleted in ^{15}N comparing to NH_3 (Freyer 1978a, b) and others that they are slightly enriched in ^{15}N comparing to NH_3 (Heaton 1987). It follows that whatever hypothesis is considered the $\delta^{15}\text{N}(\text{NH}_4^+)$ we measured is only slightly different from the initial $\delta^{15}\text{N}(\text{NO}_3)$ during heating seasons (sample group II) in Wrocław (Fig. 7). If we then compare our data with the $\delta^{15}\text{N}(\text{NH}_3)$ reported by Freyer (1978a, b) and Heaton (1987) fossil fuels combustion appears as the main vector of NH_4^+ in rainwater, a conclusion that is supported by results from earlier studies (Górka et al. 2011 and 2012).

The last process (PROCESS 3) to be tested corresponds to exchange reactions between atmospheric NH_4^+ in salts aerosols and NH_4^+ in precipitation (Fig. 7c). Atmospheric NH_4^+ in salts aerosols is mainly related to particles generated from suspension of soils (or soils fertilised with NH_4^+) or secondary inorganic aerosols (SIA) generated in the atmosphere. When under the form of ammonium nitrate (NH_4NO_3) or ammonium sulfate ($(\text{NH}_4)_2\text{SO}_4$), NH_3 is susceptible to be transported over long distances (Heeb et al. 2008). Górka et al. (2012) measured $\delta^{15}\text{N}$ in PM_{10} (particulate matter with an aerodynamical diameter $<10\text{ }\mu\text{m}$) samples from the atmosphere of Wrocław from 5.0 to 13.7‰ . It follows that dissolution of aerosols in precipitation may take place, accompanied with a nil to negligible nitrogen isotope fractionation ($\Delta^{15}\text{N}$; Fig. 7a and c).

5 Conclusions

Combined chemical, isotopic and statistical analyses provided critical information about the genesis of ions in precipitation in the atmosphere of Wrocław. A PCA analysis discriminated them into three independent factors that lead to the following conclusions:

- HCO_3^- , NO_3^- , NO_2^- , NH_4^+ and SO_4^{2-} result of emissions from direct fertilizers usage, sewage irrigation fields activity and fossil fuel combustion.
- The study of K^+ , Ca^{2+} and Mg^{2+} concentrations and PCA analysis suggest that fertilised soil, fossil fuel combustion (road traffic and industrial) and natural dust are the main sources.
- Marine aerosols, as expected, bring Na^+ and Cl^- ions to the city.

The implication and relative contributions of the processes controlling the overall budget of these ions vary following three distinct seasons: heating seasons I and II and vegetative season. The study of $\delta^{15}\text{N}(\text{NH}_4^+)$ shows that the dissolving of primary and secondary salts aerosols within the atmosphere of Wrocław is prevailing in the NH_4^+ budget. During the heating seasons (I & II) our data suggest that the main source of NH_3 in precipitation is fossil fuels combustion while during the vegetative season local fertilisers and the *Osobowice* sewage irrigation fields are dominating.

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