Contrasted spatial and long-term trends in precipitation chemistry and deposition fluxes at rural stations in France

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HIGHLIGHTS

- Atmospheric deposition highlighted contrasting spatial patterns in France.
- Inorganic compounds exhibited common trends in both wet-only and bulk deposition.
- $nssSO_4^{2-}$ concentrations primarily experienced the largest decreasing annual trend in the summer.
- A large number of stations showed an increasing trend in annual pH.
- Trends in nitrogen compounds were not linked to emission inventory changes.

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ABSTRACT

The long-distance effect of atmospheric pollution on ecosystems has led to the conclusion of international agreements to regulate atmospheric emissions and monitor their impact. This study investigated variations in atmospheric deposition chemistry in France using data gathered from three different monitoring networks (37 stations) over the period from 1995 to 2007. Despite some methodological differences (e.g. type of collector, frequency of sampling and analysis), converging results were found in spatial variations, seasonal patterns and temporal trends. With regard to spatial variations, the mean annual pH in particular ranged from 4.9 in the north-east to 5.8 in the south-east. This gradient was related to the concentration of NO_3^- and non-sea-salt SO_4^{2-} (maximum volume-weighted mean of 38 and 31 μeq l^{-1} respectively) and of acid-neutralising compounds such as non-sea-salt Ca^{2+} and NH_4^+. In terms of seasonal variations, winter and autumn pH were linked to lower acidity neutralisation than during the warm season. The temporal trends in atmospheric deposition varied depending on the chemical species and site location. The most significant and widespread trend was the decrease in non-sea-salt SO_4^{2-} concentrations (significant at 65% of the stations). At the same time, many stations showed an increasing trend in annual pH ($+0.3$ on average for 16 stations). These two trends are probably due to the reduction in SO_2 emissions that has been imposed in Europe since the 1980s. Temporal trends in inorganic N concentrations were rather moderate and not consistent with the trends reported in emission estimates. Despite the reduction in NOx emissions, NO_3^- concentrations in atmospheric deposition remained mostly unchanged or even increased at three stations ($+0.43$ μeq l^{-1} yr^{-1} on average). In contrast NH_4^+ concentrations in atmospheric deposition decreased at several stations located in western and northern areas, while the estimates of NH_3 emissions remained fairly stable. The decrease in non-sea-salt SO_4^{2-} and NH_4^+ concentrations was mainly due to a decrease in summer values and can in part be related to a dilution process since the precipitation amount showed an increasing trend during the summer. Furthermore, increasing trends in NO_3^- concentrations in the spring and, to a lesser extent, in NH_4^+

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concentrations suggested that other atmospheric physicochemical processes should also be taken into account.

1. Introduction

The atmosphere is a very complex system containing a wide range of natural compounds and anthropogenic pollutants that contribute to numerous air quality problems affecting the climate, human health and the environment (EEA, 2012). Human activities emit various compounds that influence the atmospheric composition of trace gases and aerosols. Anthropogenic emissions of sulphur (mainly SO_2) and nitrogen (mainly $NO_X = NO + NO_2$) originate from major source sectors, such as the industrial and domestic combustion of fossil fuel, road and marine transport, and agriculture (Smith et al., 2001; Monks et al., 2009; Reis et al., 2009). Natural sources of those pollutants originate from soils (NH_3, NOx, and SO_2), volcanoes (SO_2 and H_2S), seawater (sea salt, dimethylsulfide, NH_3) and lightning (NOx). Compounds emitted directly into the atmosphere (primary compounds) or those photochemically produced (secondary compounds) can be removed from the atmosphere in dry or wet depositions. The scavenging of pollutants (gas and aerosols) by clouds and rain generates changes in the chemical composition of atmospheric deposition.

The role of the chemical content of atmospheric deposition is twofold in relation to soils. First, it has severe harmful effects on the environment by depositing acidifying and eutrophying compounds, generating nutrient imbalances and changes in biodiversity. Secondly, alkaline compounds in atmospheric deposition can increase the buffering capacities of the receptor soil and are also a source of nutrients that can increase ecosystem productivity, and thus carbon sequestration (Bontemps et al., 2011; de Vries et al., 2014). The acidification and eutrophication of ecosystems have mainly been observed in Europe and North America in the past three decades (Dentener et al., 2006; Hettelingh et al., 2007; Pardo et al., 2011), and more recently in Asia (Zhao et al., 2009; Palani et al., 2011). These ecological issues are of worldwide concern (Kuylenstierna et al., 2001; Bouwman et al., 2002; Pan et al., 2013) since sulphate, ammonium and nitrate with lifetimes of about four to six days can be transported thousands of kilometres from their sources (Chin et al., 2007; Sanderson et al., 2008; Nie et al., 2013).

Several authors have explored long-term trends in the chemical composition of atmospheric deposition in Europe since 1990 (Puxbaum et al., 2002; Fowler et al., 2005a,b; Sicard et al., 2007; Fagerli and Aas, 2008; Van Der Swaluw et al., 2011; Torseth et al., 2012; Hunova et al., 2014; Vet et al., 2014; Waldner et al., 2014). Despite different sampling periods, a common decreasing trend has been observed in sulphate and hydrogen concentrations. Indeed, base cation concentrations also exhibit downward trends and this might partly explain the absence of any recovery by sensitive ecosystems from acidification and eutrophication or recovery being slower than expected (Moncoulon et al., 2007; Jonard et al., 2012). These trends have been linked to changes in precursor emission quantities, particularly from combustion or industrial processes (Probst et al., 1995; Avila and Roda, 2002). Indeed, SO_2 and NO_X emissions have been greatly reduced in Europe since 1990 (Monks et al., 2009), falling by about 60% and 30% respectively.

Under the Convention on Long-Range Transboundary Air Pollution, sulphur and nitrogen anthropogenic emissions in Europe have been mitigated by the 1999 multi-pollutants/multi-effects Gothenburg Protocol. Protocol reduction objectives were achieved for SO_2 and NH_3 in France by 2010, as well as in most European countries. However, these mitigation objectives appear to be less restrictive for NO_X as they are still being emitted in excessively high quantities (EMEP/CEIP, 2012). Consequently, nitrogen has become a pollutant of particular interest in relation to environmental issues (Wamelink et al., 2009).

For the last twenty years, several monitoring networks have established a representative database of worldwide atmospheric deposition (Vet et al., 2014). They include the National Atmospheric Deposition Program/National Trends Network (NADP/NTN) (Lehmann et al., 2007), the Clean Air Status and Trends Network (CASTNET) (Butler et al., 2005), the Canadian Air and Precipitation Monitoring Network (CAPMON) (Zbieranowski and Aherne, 2011), the European Monitoring and Evaluation Programme (EMEP) (Torseth et al., 2012), the Acid Deposition Monitoring Network in East Asia (EANET) (Totsuka et al., 2005), the International Co-operative Programme on Assessment and Monitoring of Air Pollution Effects on Forests (ICP Forests) (Lorenz, 1995) and the Atmospheric Chemistry Monitoring Network in Africa (IDAF) (Galy-Lacaux et al., 2009). In France, the long-term monitoring of atmospheric deposition has been performed by three main networks: the "Mesure et Evaluation en zone Rurale de la pollution Atmosphérique à longue distance" (MERA), the Background Air Pollution Monitoring Network (BAPMoN) and the "Charge d'Acide Totale d'origine Atmosphérique dans les Ecosystèmes Naturels Terrestres" (CATAENAT). The data from these three networks have never been investigated together at country scale.

Based on those data, the aims of this paper were (i) to set up a common database for French atmospheric deposition, (ii) to determine the amount of the inorganic component concentrations and fluxes in atmospheric deposition, (iii) to investigate the spatial pattern of these compounds, and (iv) to examine the seasonal evolution and long-term trends in atmospheric deposition over the period 1995 to 2007 for the major element concentrations and fluxes at country scale.

2. Materials and methods

2.1. Sampling sites

Table 1 presents the location and acronyms of the 37 sampling sites selected from the three French monitoring networks for the period 1995–2007. These sampling sites were distributed throughout France (Fig. 1) and represented the various climatic influences encountered (Mediterranean, Atlantic, continental and mountain influences). Monitoring stations were set up based on similar siting rirements. In particular, they were not directly exposed to industrial or urban emissions and could be considered as regional background sites. The collectors were shielded from disturbance by the erection of a fence around the station. The MERA, CATAENAT and BAPMoN stations fulfil the siting criteria defined in the EMEP manual (EMEP, 1996), the ICP Forests manual (ICPF, 2010) and the GAW Precipitation Chemistry Programme (WMO, 2004) respectively.

As part of the GAW/WMO programme (Global Atmosphere Watch/World Meteorological Organisation, http://www.wmo.int/pages/prog/arep/gaw/gaw_home_en.html), the worldwide
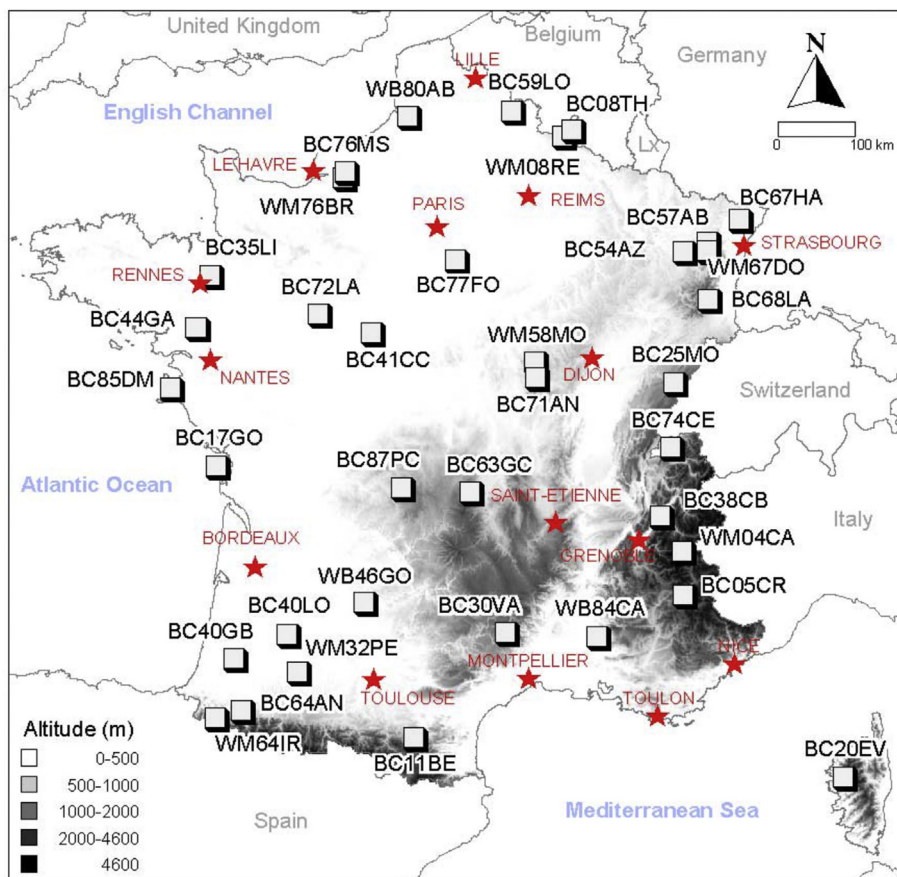
Fig. 1. Location of sampling stations. N.B.: The first letter of the acronyms defines the sampling type (B: bulk; W: wet-only); the second letter defines the network name (C: CATAENAT; M: MERA; B: BAPMoN). Some cities (>150,000 inhabitants) are highlighted in red star. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

BAPMoN network has been managed by the French National Meteorological Centre since 1977 (Cénac and Zéphoris, 1992). The goal is "to monitor the atmosphere's composition as influenced by human activities on a continental or regional scale, excluding however any significant single sources" (Kohler, 1980). The three wet-only BAPMoN sampling sites in France closed in 2007, which is the main reason why data up to 2007 was used in this study.

Within the scope of EMEP (http://emep.int/), the MERA network was set up in 1989 by the French Environment Ministry and the French Agency for Environment and Energy Management (ADEME). Its aim is to study background atmospheric pollution and especially the long-range transport of pollutants and their deposition (Plaisance et al., 1996a,b). The MERA network includes 13 wet-only remote sites in 2014, but only seven sites were effectively monitored during the 1995–2007 period.

Within the ICP Forest programme (http://icp-forests.net/), the CATAENAT network, which is part of the RENECOFOR[1] network, has been in operation in France since 1993. It is managed by the French National Forest Agency to monitor atmospheric deposition and its impact on forest ecosystems. Bulk atmospheric deposition has been sampled in 27 open-field sites close to forest monitoring sites. BC210EV is located on the island of Corsica to the south of mainland France. Detailed information about the CATAENAT network can be found in Croisé et al. (2005).

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[1] Réseau National de suivi à long terme des Ecosystèmes Forestiers.

2.2. Sampling equipment and chemical analysis

Wet-only precipitations were monitored on a weekly basis at the BAPMoN sampling sites, and on a daily basis at the MERA sampling sites. All the 27 CATAENAT sites were equipped with a weekly bulk collector (Table 1): precipitation was collected every week and kept at 4 °C in the dark before samples were pooled into four-week composites for chemical analysis. The precipitation amount was measured using a separate reference rain gauge at each sampling site. Non-automatic rain gauges were used in the CATAENAT network and automatic ones were used in the BAPMoN and MERA networks.

The CATAENAT bulk collectors consisted of a high-density polyethylene (HDPE) funnel and an HDPE bottle for rain sampling or a bag for snow sampling. Sedimenting droplets, wet and dry particles or gases were included in the bulk measurements. The BAPMoN and MERA wet-only collectors comprised a lid coupled to a sensor allowing them to open only when it rained or snowed, hence only wet deposition was collected in an HDPE bottle.

Following technical improvements, different types of wet-only collectors and sensors have been used over time by the networks. In the CATAENAT network, wet-only collectors were equipped with a Précis Mécanique sensor from 1993 to 2003 and with an Eigenbrodt IRSS 88 sensor from 2004 to 2007. In the MERA network, wet-only collectors were equipped with a Précis Mécanique sensor from 1990 to 2002, and with an Eigenbrodt RS85 sensor from 2002 to the present day. The three types of precipitation sensors have different systems to control the opening and closing of the collector. The IRSS

Table 1
List of stations in the three networks monitoring atmospheric deposition in France for the period 1995–2007.

Acronym	Networks	Type of collector	Sampling frequency	Chemical analysis frequency	Monitoring sites	Latitude	Longitude	Altitude (m)	Number of years (n)
WM76BR	MERA	Wet-only	daily	daily	Brotonne	49° 24′ N	00° 42′ E	115	13
WM05CA	MERA	Wet-only	daily	daily	Le Casset	45° 00′ N	06° 28′ E	1750	13
WM67DO	MERA	Wet-only	daily	daily	Donon	48° 30′ N	07° 08′ E	775	13
WM64IR	MERA	Wet-only	daily	daily	Iraty	43° 02′ N	01° 05′ W	1300	13
WM58MO	MERA	Wet-only	daily	daily	Morvan	47° 16′ N	04° 05′ E	620	13
WM32PE	MERA	Wet-only	daily	daily	Peyrusse-Vieille	43° 37′ N	00° 11′ E	236	13
WM08RE	MERA	Wet-only	daily	daily	Revin	49° 54′ N	04° 38′ E	390	13
WB80AB	BAPMON	Wet-only	weekly	weekly	Abbeville	50° 08′ N	01° 50′ E	70	13
WB84CA	BAPMON	Wet-only	weekly	weekly	Carpentras	44° 05′ N	05° 03′ E	99	13
WB46GO	BAPMON	Wet-only	weekly	weekly	Gourdon	44° 45′ N	01° 24′ E	259	13
BC40GB	CATAENAT	Bulk	weekly	4-week	CHP40HCT	43° 44′ N	00° 50′ W	20	13
BC59LO	CATAENAT	Bulk	weekly	4-week	CHP59HCT	50° 10′ N	03° 45′ E	149	13
BC35LI	CATAENAT	Bulk	weekly	4-week	CHS35HCT	48° 10′ N	01° 32′ W	80	13
BC41CC	CATAENAT	Bulk	weekly	4-week	CHS41HCT	47° 34′ N	01° 15′ E	127	13
BC77FO	CATAENAT	Bulk	weekly	4-week	CPS77HCT	48° 27′ N	02° 43′ E	80	13
BC71AN	CATAENAT	Bulk	weekly	4-week	DOU71HCT	47° 05′ N	04° 05′ E	650	13
BC08TH	CATAENAT	Bulk	weekly	4-week	EPC08HCT	49° 56′ N	04° 48′ E	480	13
BC63GC	CATAENAT	Bulk	weekly	4-week	EPC63HCT	45° 45′ N	02° 57′ E	950	13
BC74CE	CATAENAT	Bulk	weekly	4-week	EPC74HCT	46° 13′ N	06° 20′ E	1200	13
BC87PC	CATAENAT	Bulk	weekly	4-week	EPC87HCT	45° 48′ N	01° 48′ E	650	13
BC30VA	CATAENAT	Bulk	weekly	4-week	HET30HCT	44° 06′ N	03° 32′ E	1400	13
BC54AZ	CATAENAT	Bulk	weekly	4-week	HET54aHCT	48° 30′ N	06° 42′ E	325	12
BC64AN	CATAENAT	Bulk	weekly	4-week	HET64HCT	43° 09′ N	00° 39′ W	400	13
BC20EV	CATAENAT	Bulk	weekly	4-week	PL20HCT	42° 15′ N	08° 50′ E	1100	13
BC17GO	CATAENAT	Bulk	weekly	4-week	PM17HCT	45° 58′ N	01° 16′ W	15	13
BC40LO	CATAENAT	Bulk	weekly	4-week	PM40cHCT	44° 02′ N	00° 00′ W	150	13
BC72LA	CATAENAT	Bulk	weekly	4-week	PM72HCT	47° 44′ N	00° 20′ E	153	13
BC85DM	CATAENAT	Bulk	weekly	4-week	PM85HCT	46° 52′ N	02° 08′ W	5	13
BC44GA	CATAENAT	Bulk	weekly	4-week	PS44HCT	47° 32′ N	01° 48′ W	38	13
BC67HA	CATAENAT	Bulk	weekly	4-week	PS67aHCT	48° 51′ N	07° 42′ E	175	13
BC76MS	CATAENAT	Bulk	weekly	4-week	PS76HCT	49° 27′ N	00° 44′ E	70	13
BC05CR	CATAENAT	Bulk	weekly	4-week	SP05HCT	44° 29′ N	06° 27′ E	1360	13
BC11BE	CATAENAT	Bulk	weekly	4-week	SP11HCT	42° 52′ N	02° 06′ E	950	12
BC25MO	CATAENAT	Bulk	weekly	4-week	SP25HCT	46° 58′ N	06° 27′ E	1000	13
BC38CB	CATAENAT	Bulk	weekly	4-week	SP38HCT	45° 25′ N	06° 07′ E	1100	13
BC57AB	CATAENAT	Bulk	weekly	4-week	SP57HCT	48° 36′ N	07° 08′ E	400	13
BC68LA	CATAENAT	Bulk	weekly	4-week	SP68HCT	47° 56′ N	07° 07′ E	680	13

88 optical sensor does not need to heat the device since the sensing area is generated by infrared beams. Snow-catching pins and the heated surface of the RS85 precipitation sensor ensure the efficient collection of all kinds of atmospheric precipitation. With the Précis Mécanique electrical sensor, the residual drops from the events are dried with a resistance grid of electrode bars, ensuring collector closing. These three types of sensors have to be adjusted in order to provide reliable precipitation measurements (e.g. so as not to respond to fog or dew in the case of electrical sensors or to spider's webs in the case of optical sensors). Since an elevated temperature can lead to changes in pH (Dämmgen et al., 2005), sample solutions have been stored in a refrigerated collector since 2002 (Eigenbrodt NSA181 for MERA, Eigenbrodt UNS130 for CATAENAT and Météo France collectors for BAPMoN).

Potential biases may exist from the sampler type (wet-only vs. bulk) and from the sampling interval (daily vs. weekly). These biases depend on the station location, the type of air masses impacting the station, the surrounding terrain, meteorological conditions etc. (Butler and Likens, 1998; Thimonier, 1998; Staelens et al., 2005; Cape et al., 2009). Some biases may neutralise and cancel out the effect of other biases. For example, base cation concentrations (Ca^{2+}, Mg^{2+} and K^+) are significantly affected by coarse particles deposited on the wall of the bulk collectors, representing between 16% and 46% on average of bulk deposition (Balestrini et al., 2007). A longer sampling period affects pH and N compounds. Butler and Likens (1998) report that daily NH_4^+ concentrations are approximately 14% higher than weekly values. Precipitation sensors are known to be a critical part of the wet-only collectors. Plaisance et al. (1998) demonstrate that the collection

efficiency for those three sensors is about 90% on average. They also report significant differences in ionic compositions for H^+, Ca^{2+}, Mg^{2+} and K^+ (of about 20%), associated with the exposure of the funnel to dry deposition of particles or gases according to the system for controlling the lid opening and closing. Overall, H^+ and nssBC concentrations in the four-week bulk samples should be higher than in the daily wet-only samples, when NH_4^+ concentrations should be lower.

Over the study period, all samples were analysed for their chemical composition by the same laboratory, SGS Multilab. Data quality assurance programmes were set up within the networks. Samples were analysed for pH, major anions (Cl^-, NO_3^-, SO_4^{2-}) and cations (Na^+, K^+, Mg^{2+}, Ca^{2+}, NH_4^+). Concentrations of selected ions were obtained using various analytical techniques, as detailed in Table 2. Anions were analysed by ion chromatography for the whole period. Cations (except NH_4^+) were measured by ion chromatography or by inductively coupled plasma atomic emission spectroscopy. The method used for analysing NH_4^+ has changed several times since 1995 in order to adapt to potentially interfering substances and to avoid the use of toxic agents by the Nessler method. The SGS Multilab analytical laboratory has systematically participated to WMO/GAW intercomparisons, EMEP intercomparisons and ICP Forest intercomparison experiments. The primary goal of those experiments is to guarantee that participating laboratories that use various analytical methods are able to provide comparable measurements. According to the EMEP and GAW intercomparisons for NH_4^+ concentration, the results reported by SGS Multilab were on average within $1 \pm 15\%$ (1991–2008) and $3 \pm 14\%$ (1992–2007) of the expected values respectively.

Table 2
Type of analytical techniques applied per ion per time period by the networks.

Analytical techniques	Ions	MERA	BAPMON	CATAENAT
IC	Cl^-, $N\text{-}NO_3^-$, $S\text{-}SO_4^{2-}$	1995—2007	1995—2007	1995—2007
	Na^+, K^+, Mg^{2+}, Ca^{2+}	1995—2007	–	1995—2007
	NH_4^+	2003—2007	–	2003—2007
ICP-AES	Na^+, K^+, Mg^{2+}, Ca^{2+}	–	1995—2007	–
INDO	NH_4^+	1995—2002	1995—2002/2007	1995—2002
FIAS	NH_4^+	2002—2003	–	2002—2003
NES	NH_4^+	–	2003—2006	–

IC: ion chromatography.
ICP-AES: inductively coupled plasma atomic emission spectroscopy.
INDO: indophenol blue colorimetric method.
FIAS: flow injection atomic spectroscopy.
NES: Nessler's reagent colorimetric method.

2.3. Methods for calculation

Data were aggregated by season or by year: average values were not calculated if more than 20% of the data were missing over the considered period. Data could be missing due to a shutdown of the monitoring station or to a variety of mechanical or electrical problems. The four seasons were defined as follows: December (previous year)-February (winter), March—May (spring), June-—August (summer), and September—November (autumn).

Volume-weighted mean concentrations (C_{VWM}) of ions were computed for years and seasons using the following Equation (1):

$$C_{VWM} = \sum_{i=1}^{n}(R_i \times C_i) \bigg/ \sum_{i=1}^{n} R_i \qquad (1)$$

Annual and seasonal deposition fluxes of ions were estimated using the following Equation (2):

$$D = \sum_{i=1}^{n}(R_i \times C_i) \qquad (2)$$

where n is the number of individual samples, C_i the concentration of the ions and R_i the precipitation measured by a reference rain gauge. The precipitation amount associated with invalid samples was used to calculate the annual precipitation amount. If the precipitation amount was missing, samples were not accounted for.

Sodium ion was used to estimate the non-sea-salt (nss) ionic concentrations from the ionic ratio of sea water expressed in eq/eq, e.g. the ratio for SO_4^{2-}/Na^+ is 0.12, $Mg^{2+}/Na^+ = 0.228$, $K^+/Na^+ = 0.021$, $Ca^{2+}/Na^+ = 0.043$ (Keene et al., 1986). The concentrations of non-sea-salt base cations (nssBC) were obtained by summing the $nssMg^{2+}$, $nssK^+$ and $nssCa^{2+}$ concentrations (in $\mu eq\ l^{-1}$).

pH was measured using a pH meter, then transformed to H^+ to calculate the volume-weighted mean concentration. Finally an average pH was calculated using the volume-weighted mean H^+ concentration.

2.4. Statistical trend analysis

Numerous methods can be applied for the study of long-term trends in air quality and atmospheric deposition chemistry. Since data distribution is not normal and robust, the non-parametric seasonal Mann Kendall test is considered to be the most appropriate and powerful for detecting linear trends (Marchetto et al., 2013). As this study showed, differences between a seasonal Mann Kendall test and a Mann Kendall test for long series were negligible. Therefore, a Mann Kendall test was performed over the 13-year period (Gilbert, 1987) to determine whether a trend was significant or not, using either yearly data or seasonal data. Additionally, the Sen's method (Sen, 1968) was used to calculate the trend slope. The software tool MakeSense (Salmi et al., 2002) was used to detect and estimate annual and seasonal trends in atmospheric deposition for each sampling site. The probability of observing a trend was computed using the Z-score. The trend was considered as statistically significant when the level of significance was above 90%.

3. Results and discussion

3.1. Spatial distribution and seasonal variability

3.1.1. Precipitation

Precipitation has a considerable influence on the deposition amount of inorganic species. Below-cloud scavenging (washout) of aerosol and gases leads to higher concentrations in lower precipitation samples (Ulrich et al., 1998; Anderson and Downing, 2006). After the washout, concentrations result mainly from the rainout of clouds, leading to lower concentrations in higher precipitation samples. The mean annual precipitation was 1109 ± 372 mm across all sampling sites (n = 37, Fig. 2). Spatial differences were observed between sampling sites. Annual precipitation was high in the mid and high French mountains. A southern site, located in the area of the Cévennes Mountains, received the highest annual precipitation (BC30VA site, mean 2400 mm). It was characterised by strong convective precipitation, which usually occurred in autumn (Vidal et al., 2010). The enhancement of precipitation by orographic effects has also been highlighted in the Alps by Frei and Schär (1998). Low annual precipitation was recorded in the southern and western areas, which are influenced by the Mediterranean and marine west coast climates respectively.

A high variability in seasonal precipitation was recorded (Fig. 3). The seasonal variations in mountain and continental sites reached a maximum in the summer (e.g. at BC74CE 351 mm for the three summer months) and a minimum in late winter and spring (e.g. at BC63GC 274 mm for the three spring months). The monthly pattern on plain sites was the opposite for mountain sites. For example, the driest month was observed in June at the BC85DM site (105 mm for the three summer months) located on the western coast, while the rainiest months occurred between September and December (247 mm for the autumn months).

3.1.2. SO_4^{2-} ions

The non-sea-salt sulphate ion ($nssSO_4^{2-}$) is representative of non-marine sources of sulphate such as urban and industrial activities (Lim et al., 2014; Watmough et al., 2014). The annual VWM concentrations of $nssSO_4^{2-}$ ranged from 16 to 38 $\mu eq\ l^{-1}$ (Fig. 2). The highest concentration of $nssSO_4^{2-}$ was found in southern and north-
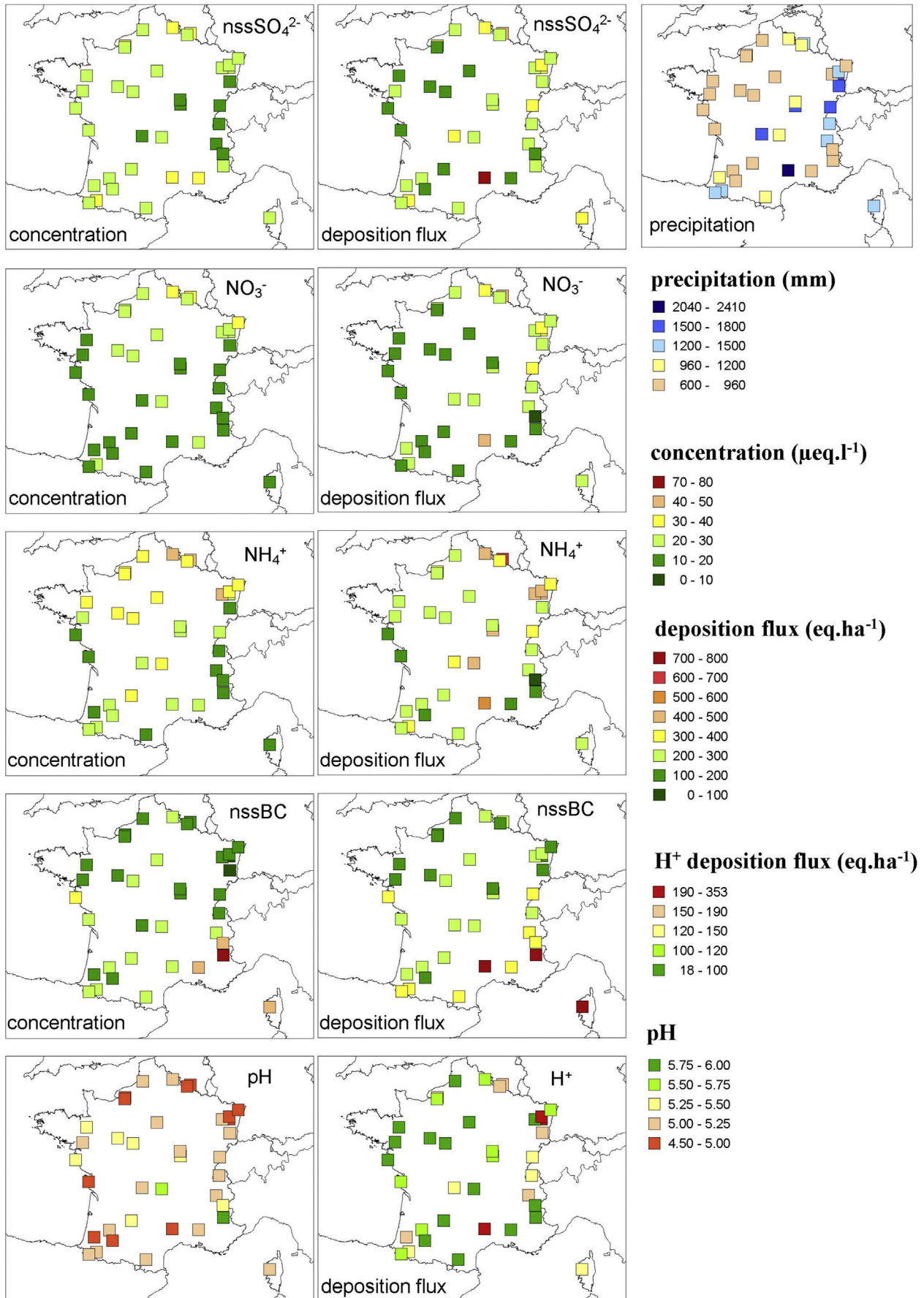
Fig. 2. Volume-weighted mean concentrations and deposition fluxes of non-sea-salt SO_4^{2-}, NO_3^-, NH_4^+, non-sea-salt base cation, H^+, mean pH (from volume-weighted mean H^+ concentrations) and annual precipitation in France for the period 1995–2007.
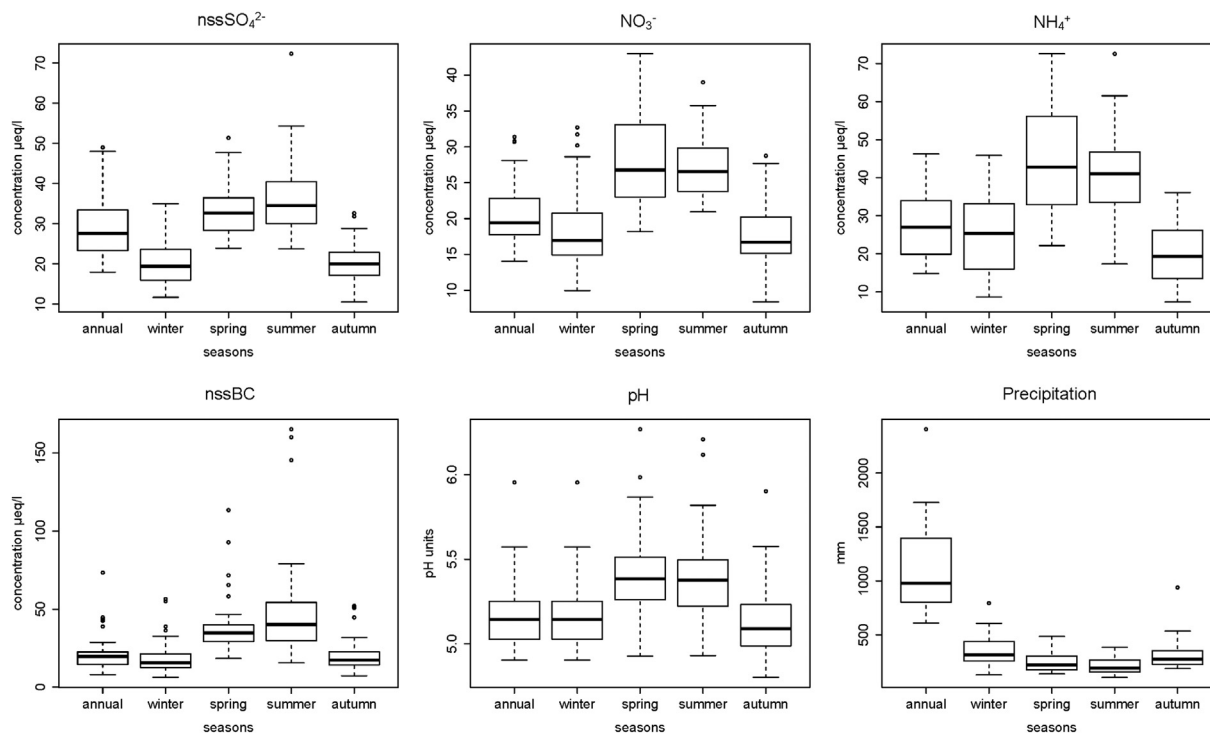
Fig. 3. Annual and seasonal volume-weighted mean concentrations of non-sea-salt SO_4^{2-}, NO_3^-, NH_4^+, non-sea-salt base cation, mean pH (from volume-weighted mean H^+ concentrations) and precipitation in France for the period 1995–2007 (n = 37). The plot whiskers extend to 1.5 times the interquartile range from the box. The bottom and top of the box are the 25th and 75th percentile respectively, and the band inside the box is the 50th percentile.

eastern France. Several studies have identified the occurrence of $nssSO_4^{2-}$ in these parts of France and in neighbouring countries (Probst et al., 1990; Sanusi et al., 1996; Ulrich et al., 1998; Marquardt et al., 2001; André et al., 2007; Sicard et al., 2007). Spatial distribution of $nssSO_4^{2-}$ deposition was partly influenced by high precipitation (Spearman coefficient 0.82, p < 0.001), particularly at the eastern Alpine relief and Cévennes sites, while the influence of concentrations was not significant (Spearman coefficient 0.19, p = 0.25).

Seasonal $nssSO_4^{2-}$ concentrations were higher in the spring (mean 34 µeq l^{-1}) and summer (mean 37 µeq l^{-1}) than in the autumn and winter (both mean 21 µeq l^{-1}) (Fig. 3). This can be attributed to a larger formation of sulphuric acids due to enhanced photochemistry and a higher conversion rate in the warm season (Calvert and Stockwell, 1984). These seasonal patterns can also be related to seasonality in anthropogenic aerosols and primary emissions (Soner Erduran and Tuncel, 2001; Freney et al., 2011; Bourcier et al., 2012).

3.1.3. NO_3^- ions

The nitrate ion is also an important contributor to precipitation chemistry. The mean of VWM concentrations of NO_3^- for all sampling sites was 21 ± 4 µeq l^{-1} (Fig. 2). The highest annual VWM NO_3^- concentration was observed at a north-eastern site (31 µeq l^{-1}). Annual VWM concentrations of NO_3^- in the present study were similar to those found by Staelens et al. (2005) in Belgium. A higher annual VWM NO_3^- concentration was observed in northern France (above 20 µeq l^{-1}) than in southern France (below 20 µeq l^{-1}). In southern France, NO_3^- concentrations were even lower than $nssSO_4^{2-}$ concentrations (Fig. 2). The NO_3^--to-$nssSO_4^{2-}$ ratio is an indicator of the relative contribution of sulphuric acids (H_2SO_4) and nitric acids (HNO_3) to the acidity of rainwater (Galloway et al., 1982). The low NO_3^--to-$nssSO_4^{2-}$ ratio in the southern part of

France (ranging from 1 to 1.5) indicated that SO_4^{2-} was the greatest contributor to acidity. Spatial distribution of NO_3^- deposition showed higher values in the northern and eastern parts of France, with the exception of the maximum observed at the BC30VA site in the Cévennes Mountains (Fig. 2).

Seasonal variability in NO_3^- concentrations was similar to SO_4^{2-} concentrations (Fig. 3). Higher values in the spring (mean 28 µeq l^{-1}) and summer (mean 27 µeq l^{-1}) can be attributed to a larger formation of HNO_3 (Calvert and Stockwell, 1984). However, Bourcier et al. (2012) show that the levels of NO_3^- particles are highest during the cold season. NO_3^- particles are primarily in the form of ammonium nitrate (NH_4NO_3), which is thermally stable during the cold season (Mozurkewich, 1993). The predominant forms in the warm season are coarser (Bourcier et al., 2012) and some authors suggest an association of NO_3^- with Ca^{2+} or Na^+ (Rodriguez et al., 2004).

3.1.4. NH_4^+ ions

NH_4^+ ions measured in atmospheric deposition can originate from ammonium aerosols, which are produced by the association of NH_3 with either NO_X or SO_X, mostly emitted by anthropogenic activities. When considering all the sampling sites, the mean annual VWM concentration of NH_4^+ was 28 ± 9 µeq l^{-1} (Fig. 2). Ranging from 13 to 46 µeq l^{-1}, a spatial difference was identified between northern and southern regions. Other studies investigating atmospheric deposition in France and Europe have found similar levels of NH_4^+ concentrations (Plaisance et al., 1996a,b; Sicard et al., 2007; Angeli et al., 2009; Celle-Jeanton et al., 2009; Vet et al., 2014). The NH_4^+-to-SO_4^{2-} ratio was higher than 1 in most of the northern sampling sites, suggesting that NH_3 is abundant enough to neutralise all the H_2SO_4 and to form $(NH_4)_2SO_4$ particles. Thus, a fraction of NH_3 can remain in the gas phase, available to form NH_4NO_3 in the aerosol phase. Such behaviour has also been

observed in the USA by Lehmann et al. (2007), in China by Xie et al. (2008) and in India by Behera and Sharma (2010). The largest annual NH_4^+ deposition flux was above 400 eq ha^{-1} yr^{-1}, recorded at the Cevennes BC30VA site. About 300 eq ha^{-1} yr^{-1} of NH_4^+ deposition was recorded in the north-eastern part. This spatial pattern was strongly influenced by precipitation (Spearman coefficient 0.62, p < 0.001) and concentration (Spearman coefficient 0.63, p < 0.001). However, the correlation with concentration could be influenced by the high number of bulk samplers (27 out of 37 stations). High NH_4^+ deposition fluxes in the eastern part of France matched the spatial distribution of annual SO_4^{2-} and NO_3^- deposition fluxes.

Seasonal variability in NH_4^+ concentrations revealed that the maximum was recorded during the spring (mean 46 μeq l^{-1}) and summer (mean 42 μeq l^{-1}) (Fig. 3). Similar variations in NH_4^+ have been observed in Spain by Calvo et al. (2012). The increase in NH_4^+ concentrations in the spring and summer might result from the volatilisation of NH_3 from fertiliser application during crop growth (spring) and the spread of manure in late summer. Previous studies have already observed a springtime increase in atmospheric deposition of NH_4^+ due to agricultural activities (Anderson and Downing, 2006; Avila et al., 2010). Moreover, the seasonal variability in NH_3 emissions can be explained by a combination of agricultural practices and weather conditions (Loubet et al., 2009). The link between the seasonal variability in NH_4^+ and NO_3^- and in $nssSO_4^{2-}$ is likely to be due to NH_4NO_3 and $(NH_4)_2SO_4$ in the aerosol phase.

3.1.5. nssBC ions

The non-sea-salt base cation concentrations ($nssBC = nssCa^{2+} + nssMg^{2+} + nssK^+$) were represented on average by 84% of the non-sea-salt Ca^{2+} concentrations, 6% of the non-sea-salt Mg^{2+} concentrations and 10% of the non-sea-salt K^+ concentrations. On average, the annual VWM concentrations of nssBC were 24 ± 14 μeq l^{-1} (Fig. 2). The highest annual VWM concentration of nssBC was observed in south-eastern France. A large amount of nssBC concentrations due to $nssCa^{2+}$ frequently originates from local resuspension or long-range sources of wind-blown mineral dust (Ulrich et al., 1998). The Sahara desert provides most of the non-local mineral dust in south-western Mediterranean regions, including the southern part of France (Avila et al., 1998; Rogora et al., 2004; Calvo et al., 2010; Izquierdo et al., 2012; Vincent et al., 2015). Evidence of Ca^{2+} ions originating from Saharan events in atmospheric deposition has also been found in Belgium by Vanderstraeten et al. (2008). Higher concentrations of nssBC than of NH_4^+ in south-eastern France suggest that nssBC ions were the main contributors to neutralising acidity in rainwater in this part of France. Deposition fluxes of nssBC showed a strong north-south gradient, more influenced by concentration (Spearman coefficient 0.72, p < 0.001) than by precipitation amount (Spearman coefficient 0.32, p < 0.1).

Seasonal variability in nssBC concentrations highlighted that the maximum was recorded in the spring (mean 50 μeq l^{-1}) (Fig. 3). The high concentrations of nssBC, mostly Ca^{2+}, can be associated with human activities, local soil erosion and frequent intrusions of Saharan dust, with specific intense episodes in the spring and summer (Calvo et al., 2012).

3.1.6. pH and H^+ deposition flux

Natural rainwater acidity (pH from 5.0 to 5.6) can be generated by atmospheric CO_2, NO_X, SO_2 and others acidifying trace gases emitted by natural sources and dissolved in cloud droplets (Galloway and Likens, 1976; Galloway et al., 1982). The mean annual pH for all sampling sites was 5.13 ± 0.19 (Fig. 2). Spatial distribution of pH values was influenced by air mass origin. The highest value of

5.81 was recorded at a southern-eastern sampling site and reflected the influence of mineral dust, as discussed above. The sampling sites located in north-eastern France were characterised by acidic precipitations (the lowest pH value was 4.87). This region of France has been particularly exposed to acid rain since it is frequently under the influence of air masses coming from heavily polluted urban and industrial areas, by long-range transport or medium-range surroundings (Probst et al., 1990; Charron et al., 2000). Annual values of the fractional acidity, as defined by Balasubramanian et al. (2001), varied from 0.03 (BC05CR, alpine site) to 0.29 (WM67DO, eastern site) with an average of 0.17 ± 0.05, indicating that about 80% of the acidity was neutralised by alkaline ions. The highest deposition fluxes of H^+ were also found in north-eastern France, with the exception of an excess of H^+ deposition (about 350 eq ha^{-1} yr^{-1}) at the BC30VA Cévennes site, which is characterised by very high annual precipitation.

Interactions between SO_4^{2-}, NO_3^- and also NH_4^+ or mineral dust controlled seasonal variability in pH. Low values of pH were found in the winter (min 4.90) and autumn (min 4.80) whereas SO_4^{2-} and NO_3^- concentrations were at their minimum (Fig. 3). The highest pH was observed during the warm season (spring and summer), suggesting that NH_4^+ and Ca^{2+} were slightly more available than during the cold season. Indeed, NH_3 emissions are at their maximum in the spring and have a strong seasonal variability, which influences the neutralisation of rainwater acidity. Primary SO_2 and NO_X are mainly emitted in the cold season but clean air masses from the North Atlantic dilute the air pollutants during winter, leading to lower concentrations in atmospheric deposition. Frequent temperature inversions during the spring provide a very stable boundary layer and an efficient accumulation of pollutants (Lenhart and Friedrich, 1995), which is commonly associated with polluted air masses coming from eastern Europe.

3.2. Long-term annual and seasonal trends

3.2.1. Precipitation

Not significant trends in annual precipitation were found at 67% of the sampling sites (Fig. 4). Overall, few significant decreasing trends were detected in southern France, with slopes ranging from −15 mm yr^{-1} to −36 mm yr^{-1} (p < 0.1, n = 4). These decreasing trends were difficult to compare to other studies because they often considered longer periods (Brunetti et al., 2001; Moisselin et al., 2002; Klein Tank and Konnen, 2003; Buishand et al., 2013).

On a seasonal basis, some significant increasing precipitation trends were observed in the summer (Fig. 5), particularly in the northern part of France (+9.5 ± 0.7 mm yr^{-1}, n = 6). In contrast, precipitation significantly decreased in the autumn at a few stations (−16.9 ± 13.4 mm yr^{-1}, n = 4). Summertime increasing trends in precipitation have also been reported by several authors in The Netherlands (Lenderink et al., 2009; Buishand et al., 2013). Climate modelling suggests that the changes in precipitation patterns along the North Sea and Atlantic coasts are influenced by changes in sea surface temperature, probably due to changes in atmospheric circulation (Haren et al., 2012).

3.2.2. SO_4^{2-} ions

From 1995 to 2007, annual $nssSO_4^{2-}$ concentration and deposition declined by 30 and 40% (averaged at 37 sampling sites) respectively. These statistically significant decreases were recorded at about 70% of the sampling sites (Fig. 4). Significant decreasing trends in $nssSO_4^{2-}$ concentrations were found with an average of −0.67 ± 0.31 μeq l^{-1} yr^{-1} (n = 24). The decrease in annual $nssSO_4^{2-}$ deposition was also homogenous and reached −9.2 ± 3.3 eq ha^{-1} yr^{-1} (n = 27). These results are consistent with those of a similar study on rural French sampling sites for the
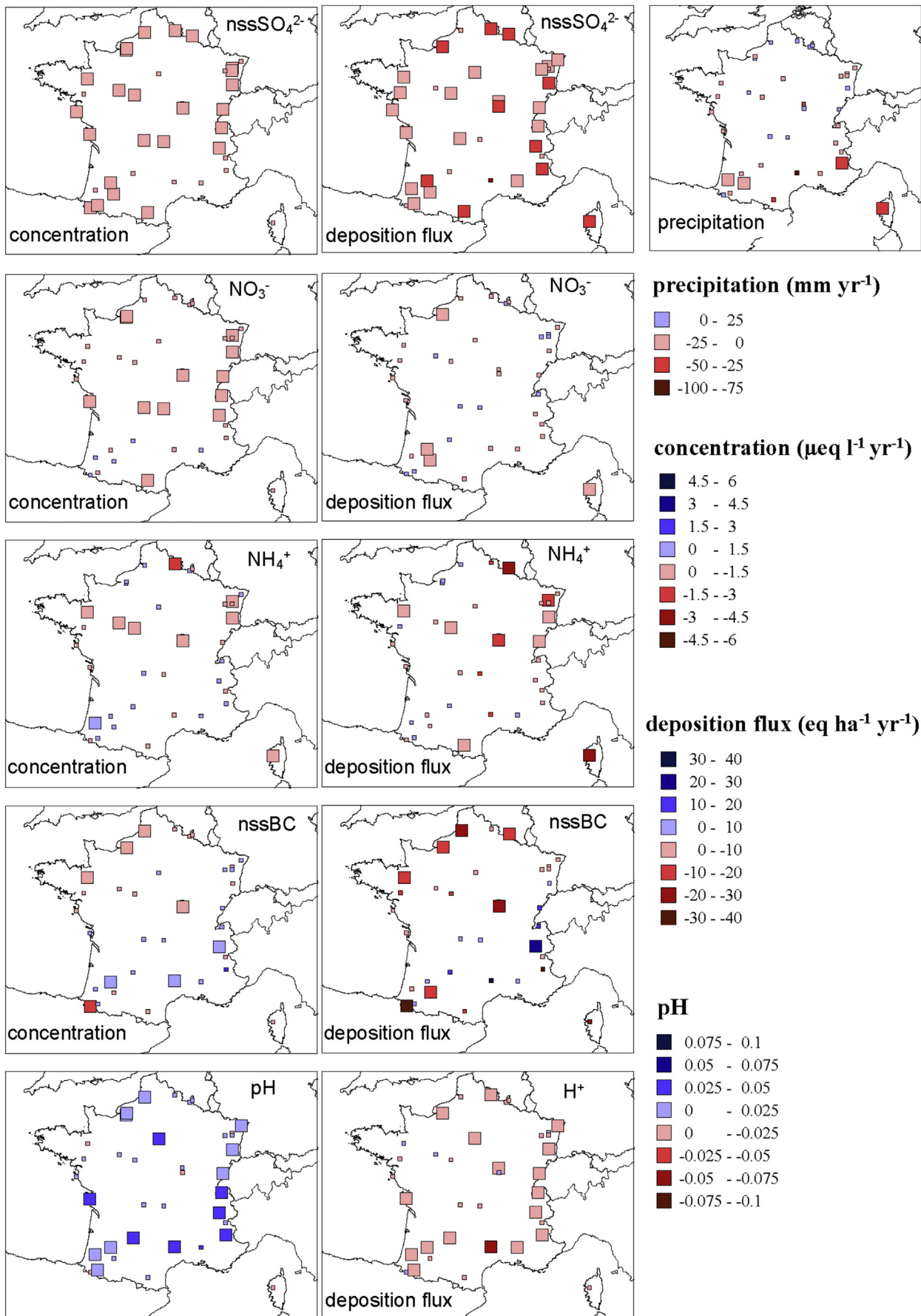
Fig. 4. Annual trends in volume-weighted mean concentrations and deposition fluxes of non-sea-salt SO_4^{2-}, NO_3^-, NH_4^+, non-sea-salt base cation, H^+, mean pH (from volume-weighted mean H^+ concentrations), and annual precipitation for the period 1995–2007 in France. The large squares indicate that the trends are significantly different from 0 at a 0.1 confidence level.
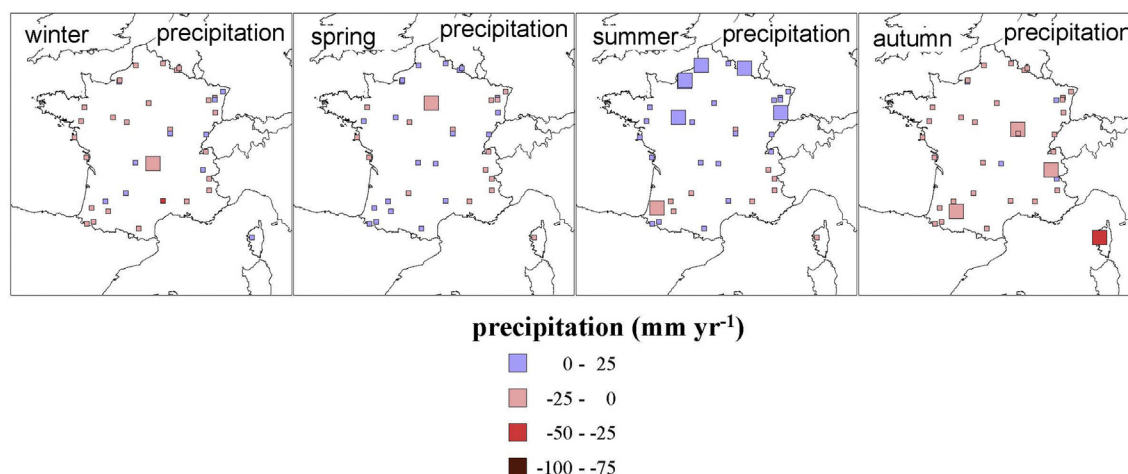
Fig. 5. Seasonal trends in mean precipitation for the period 1995–2007 in France. The large squares indicate that the trends are significantly different from 0 at a 0.1 confidence level.

period 1990–2003 (Sicard et al., 2007). To a larger extent, the results of the present study also agree with those reported for other European countries (Fowler et al., 2005a,b; Monks et al., 2009; Avila et al., 2010; Van Der Swaluw et al., 2011; Torseth et al., 2012) and North American countries (Lehmann et al., 2007; Zbieranowski and Aherne, 2011). The long-term trend of a reduction in annual $nssSO_4^{2-}$ concentrations could be linked to that in SO_2 emissions, which have decreased by 65% during the period 1990–2009, according to EMEP data (Vestreng et al., 2007; Monks et al., 2009; EMEP/CEIP, 2012).

The greatest significant absolute reductions in seasonal $nssSO_4^{2-}$ concentrations occurred in the summer (Fig. 6a) when $nssSO_4^{2-}$ concentrations were at their seasonal maximum (-1.68 ± 0.7 μeq l^{-1} yr^{-1}, n = 26). However, a significant decline in seasonal deposition of $nssSO_4^{2-}$ occurred irrespective of the season.

3.2.3. NO_3^- ions

Unlike the reductions for SO_4^{2-}, concentrations and depositions of NO_3^- mostly remained steady on an annual basis from 1995 to 2007 (Fig. 4). Moreover, a significant increase in annual concentrations was observed for some sampling sites ($+0.43 \pm 0.23$ μeq l^{-1} yr^{-1}, n = 3), while significant downward trends were observed in annual deposition for other sampling sites (-3.75 ± 1.91 eq ha^{-1} yr^{-1}, n = 4). Rogora et al. (2006) and Waldner et al. (2014) report that the lack of a significant decrease in NO_3^- concentrations can be related to the slow general decrease in anthropogenic emissions of NO_X in Europe. The decrease in European NO_X emissions has been estimated to be 31% over the period 1990–2009 (Monks et al., 2009; EMEP/CEIP, 2012). However, although the principal continental emission sector of NO_X is road transport (Vestreng et al., 2009), atmospheric emissions of NOx from international shipping dramatically increased between 1995 and 2007 (Derwent et al., 2005; Endresen et al., 2007; Eyring et al., 2010). This additional source could have an impact on NO_3^- concentrations. Moreover, Marchetto et al. (2013) suggest that the nonlinearity with emission trends can be multifactorial: i) changes in emissions (new or unknown emission sources not included in emission inventories); ii) evolutions in wet and dry partitioning of sulphur and nitrogen content (increasing dry deposition velocity of SO_2 due to the deposition of NH_3 (Fowler et al., 2007) and increase in NO_3^- deposition due to an increase in nitrate aerosol and greater transport (Irwin et al., 2002)); and iii) modification in the rate of atmospheric oxidation (changes in the limiting reagent for the

formation of nitrate aerosol (Pun and Seigneur, 2001)).

When considering seasonal trend results, NO_3^- concentrations showed a tendency to be higher in the winter, spring and autumn (Fig. 6b). Only a few southern sites showed a significant trend in the spring, with an average of $+0.67 \pm 0.24$ μeq l^{-1} yr^{-1} (n = 6). In contrast, NO_3^- concentrations significantly declined in the summer by on average -0.84 ± 0.24 μeq l^{-1} yr^{-1} (n = 8, p < 0.1), especially at the northern sites. Estimated atmospheric emissions of NO_X did not show strong seasonality since the major source of NOx pollution is road transport. The major factor affecting the seasonal trends of NO_3^- concentrations can be linked to atmospheric oxidising conditions due to the enhancement of the oxidation rate by OH radicals in the summer (Calvert and Stockwell, 1984). The cause of the differentiation in the trends of NO_3^- concentrations between northern and southern sites is still unclear, but the decrease observed in the summer for the northern sites can partly be related to a dilution process by the precipitation amount. Indeed, as previously mentioned, the summer precipitation showed a tendency to be higher in northern regions, and the higher the amount of precipitation, the more diluted the concentrations due to the higher contribution of the rainout of clouds which is less concentrated than the washout (Jaffrezo et al., 1990; Alastuey et al., 2001; Aikawa and Hiraki, 2009). However, a multi-factor cause can also be evoked, such as changes in temperature, photochemical rate or equilibrium towards more particulate ammonium nitrate.

Major decreasing trends in NO_3^- deposition were recorded in the summer and autumn. Seasonal changes in NO_3^- deposition were influenced by seasonal changes in precipitation, as with the southern sites in the summer. As a result, these seasonal changes were not always in agreement with seasonal changes in NO_3^- concentrations.

3.2.4. NH_4^+ ions

In terms of NH_4^+ concentration in precipitation, only nine bulk sampling sites showed a statistically significant decrease (-0.75 ± 0.6 μeq l^{-1} yr^{-1} on average) (Fig. 4). This small change was observed mostly in the western and northern areas of France. As NH_3 emissions only decreased by 29% for the period 1990–2009 in Europe (Monks et al., 2009; EMEP/CEIP, 2012), which is much lower than the decrease in SO_2 emissions (65%), the annual NH_4^+ concentrations in precipitation were not expected to change significantly. Fagerli and Aas (2008) report that trends in modelled annual concentrations of NH_4^+ at sampling sites in Europe can be
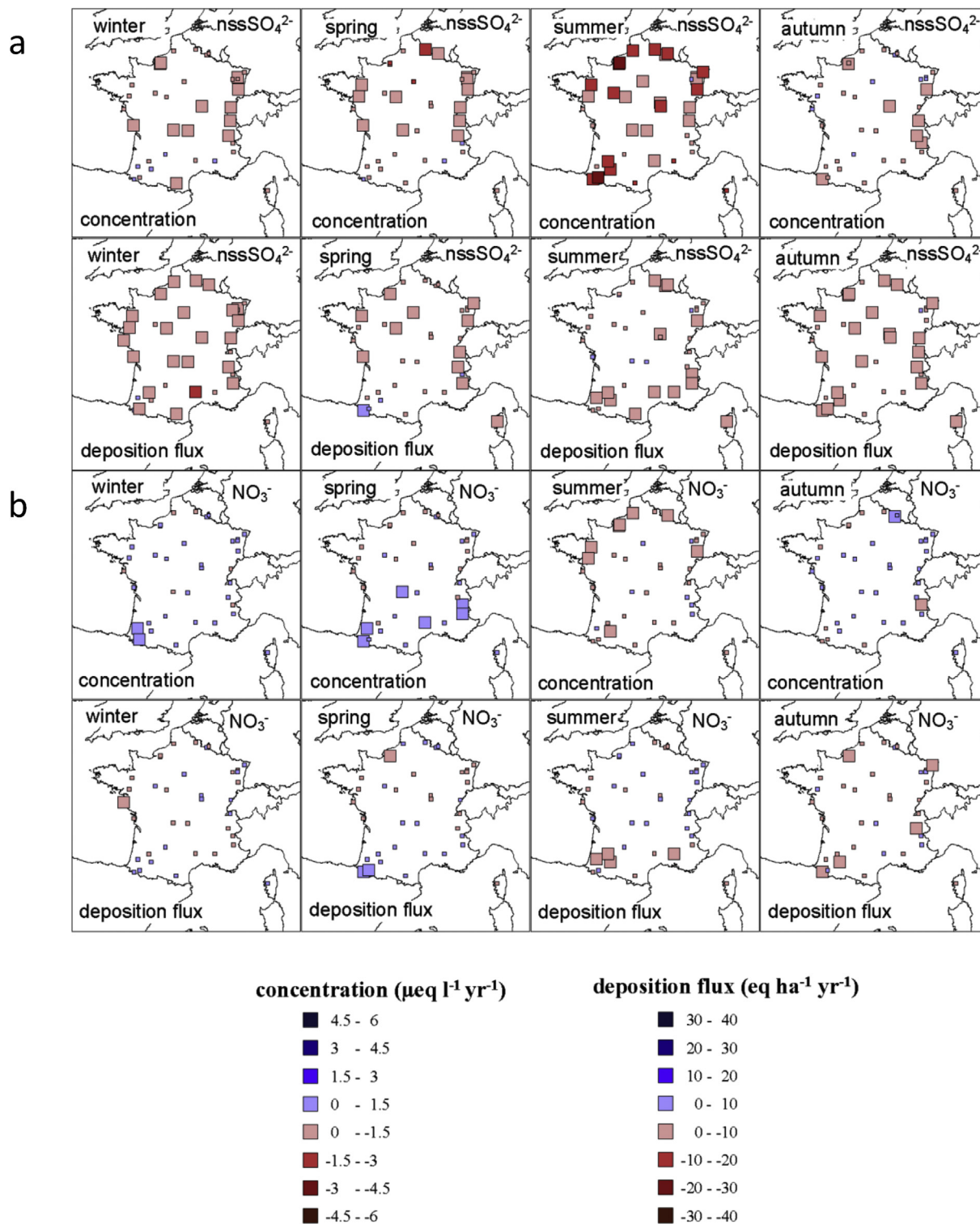
Fig. 6. Seasonal trends in volume-weighted mean concentrations and deposition fluxes for the period 1995—2007 in France: (a) non-sea-salt SO_4^{2-}, (b) NO_3. The large squares indicate that the trends are significantly different from 0 at a 0.1 confidence level, (c) NH_4^+, (d) non-sea-salt base cation. The large squares indicate that the trends are significantly different from 0 at a 0.1 confidence level, (e) mean pH, (f) H^+. The large squares indicate that the trends are significantly different from 0 at a 0.1 confidence level.

influenced by trends in atmospheric emissions of SO_2. In Sweden, a strong decrease in particulate ammonium concentration has been linked to a decrease in particulate $nssSO_4^{2-}$ concentration since the 1990s, while ammonia concentration has increased (Ferm and Hellsten, 2012). Indeed, more NH_3 may be available to form long-range transported secondary particles. An increase in the formation of NH_4NO_3 by neutralising HNO_3 can therefore explain the lack of trends in annual concentrations of NO_3^- and NH_4^+. Trends in deposition of NH_4^+ showed a slight general decrease for the period 1995—2007 at 28 sampling sites, but the decrease was significant
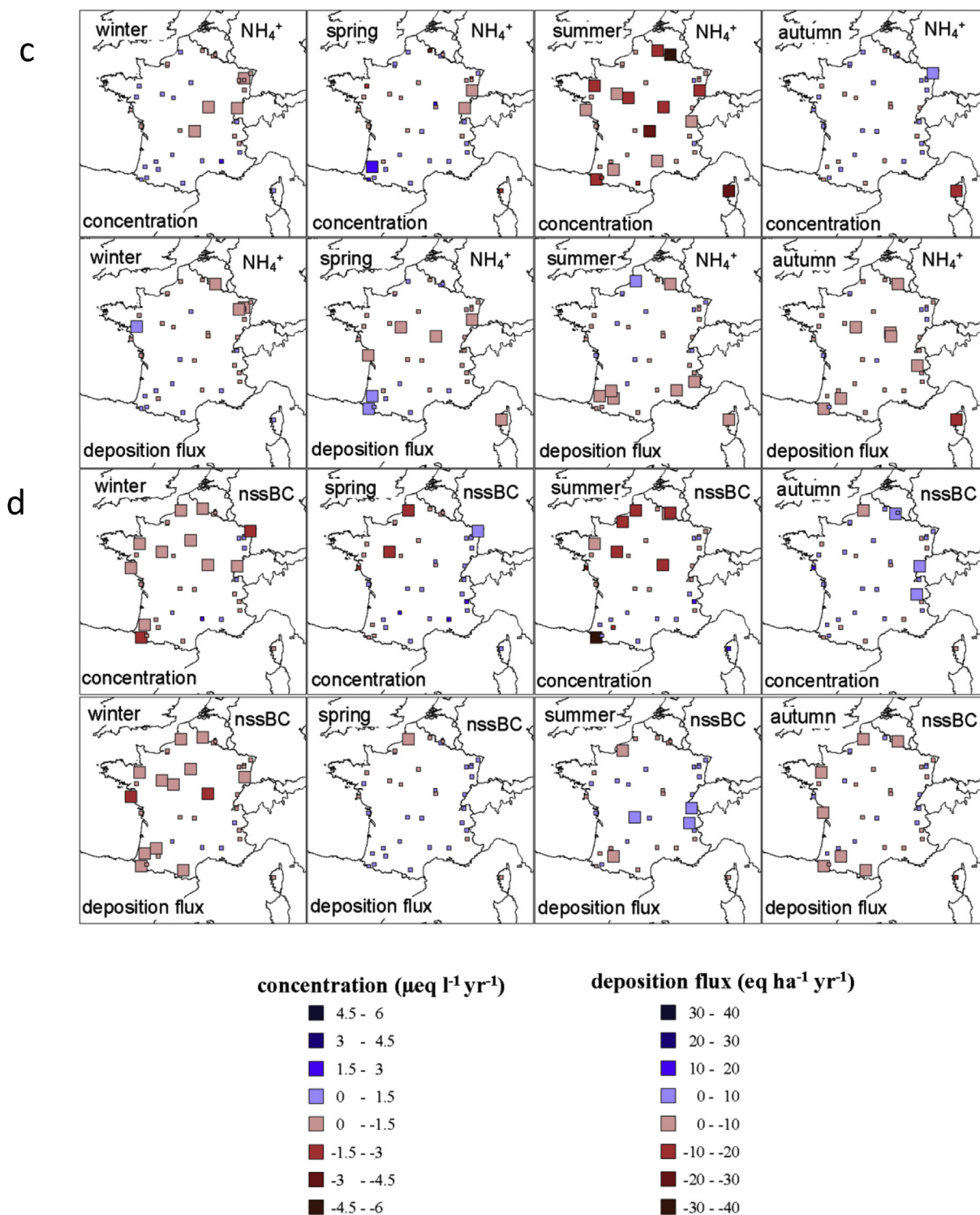
Fig. 6. (*continued*).

only at nine sampling sites (on average -12 ± 6.7 eq ha^{-1} yr^{-1}).

On a seasonal basis, significant decreases in NH$_4^+$ concentrations mostly occurred during the summer in both wet-only and bulk sampling sites (Fig. 6c) with an average of -2.3 ± 1.1 eq l-1 yr^{-1} (n = 14). Decreases in concentrations of NH$_4^+$ and nssSO$_4^{2-}$ were observed during the summer, while significant increases in concentrations of NH$_4^+$ and NO$_3^-$ occurred in the spring. These results suggest an evolution in temporal variability in (NH$_4$)$_2$SO$_4$ and

NH$_4$NO$_3$ particles. Seasonal deposition of NH$_4^+$ decreased in the autumn, spring and summer, partly due to decreasing trends in precipitation.

3.2.5. nssBC ions

No homogeneous changes were observed in annual nssBC concentrations (Fig. 4), with annual nssBC concentrations significantly decreasing and increasing at only five and three sites
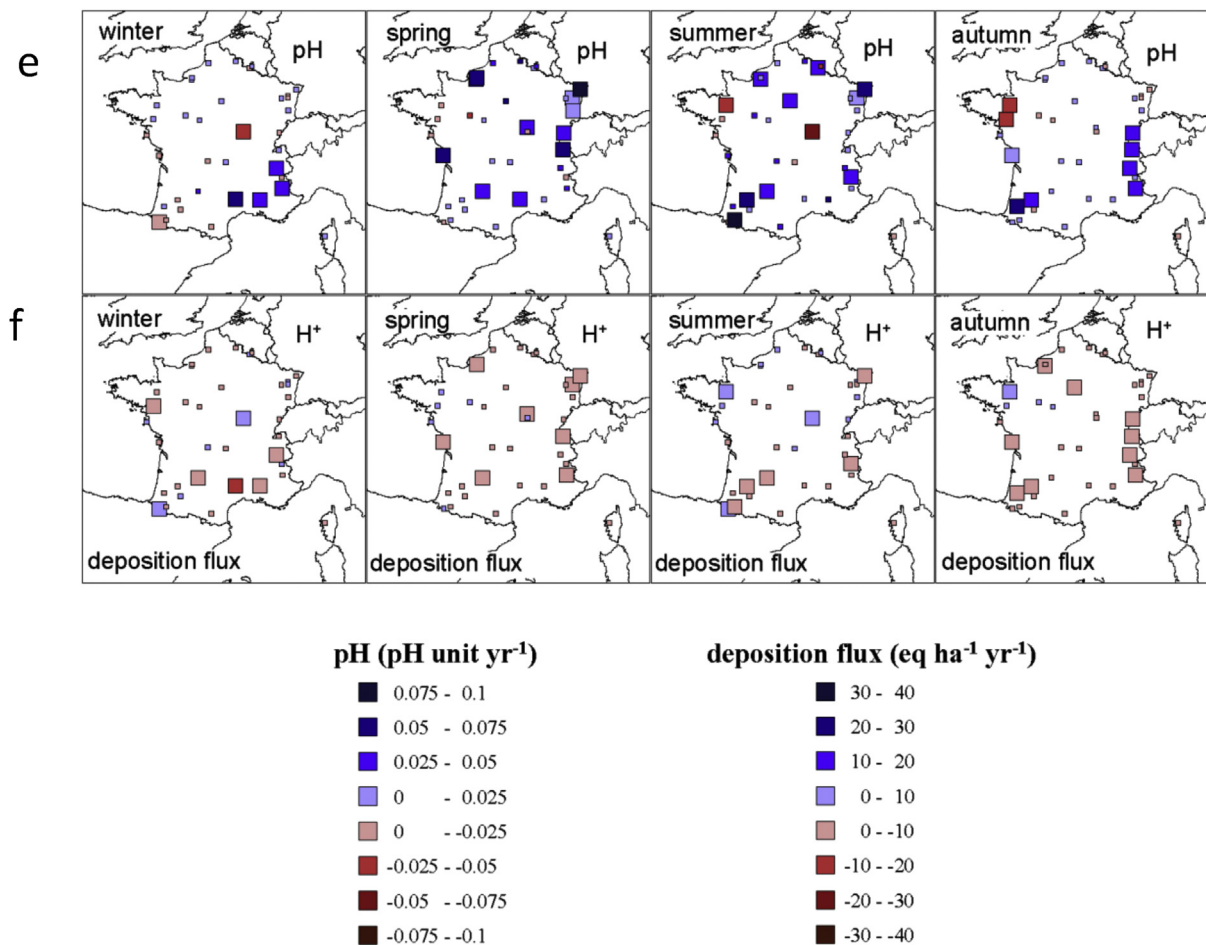
Fig. 6. (continued).

respectively (-0.33 ± 1.31 μeq l^{-1} yr^{-1}, n = 8). Trends in annual nssBC concentrations were driven by the main base cation nssCa^{2+}. Increasing trends in nssBC concentrations concerned stations located in south-eastern France. This might mean that Saharan dust influence increased at these sampling sites for the period 1995–2007, as suggested by Rogora et al. (2006) in Italy for the last 15–20 years. As with NH$_4^+$, decreasing annual trends in the annual nssBC deposition were related to decreasing precipitation trends (-13 ± 17 eq ha^{-1} yr^{-1}, n = 8).

Trends in seasonal nssBC concentrations exhibited stronger reductions in the summer than in the winter (Fig. 6d), by -2.3 ± 1.1 μeq l^{-1} yr^{-1} at eight sites and -1.0 ± 0.6 μeq l^{-1} at 12 sites (p < 0.1) respectively. The significant decreasing trends in concentrations were mostly observed at north-western sampling sites, where precipitation had increased, as a result of the dilution process (Aikawa and Hiraki, 2009). In contrast, seasonal increasing trends in nssBC concentrations were found in the autumn (statistically significant at two bulk Alpine sampling sites), while seasonal precipitation showed decreasing trends at one of those sampling sites. A lower precipitation amount implies higher concentrations in the sample due to an increase in the contribution of washout (Aikawa and Hiraki, 2009). Additionally, Moulin et al. (1998) demonstrate that Saharan dust transport is constrained by intense precipitation events during the winter and autumn in the Mediterranean and Maghreb regions. Although the main seasons of Saharan dust production are the spring and summer, an increase in autumn nssBC concentrations might be explained by greater dust

transport over Europe during the cold season due to possible modifications in atmospheric circulation patterns (Chiapello and Moulin, 2002).

3.2.6. pH and H$^+$ deposition flux

Changes in annual pH were fairly similar among the sampling sites (Fig. 4). Annual pH increased at many sampling sites by 0.3 ± 0.1 pH unit over the period 1995–2007; this increase was significant at 16 sampling sites. The main factors governing the trends of pH were the nssBC, NH$_4^+$, nssSO$_4^{2-}$ and NO$_3^-$ trends. For the northern acidic sites near the Belgian border, not significant trend in annual pH was observed, suggesting that decreases in concentrations of nssSO$_4^{2-}$ and NO$_3^-$ were not enough to induce a greater increase in annual pH. Moreover concomitant decreases in NH$_4^+$ concentrations provided not significant changes in annual pH. These results were consistent with recent research reporting that deposition fluxes of H$^+$ decrease on an annual basis in European precipitation (Torseth et al., 2012; Marchetto et al., 2013; Vet et al., 2014). As deposition is linked to concentration by precipitation, a significant H$^+$ trend was therefore influenced by the changes in annual precipitation (-5.77 ± 4.34 eq ha^{-1} yr^{-1}, n = 17).

Most of the sampling sites were characterised by an increase in pH in the summer (n = 28), rising by 0.6 ± 0.3 for the significant increases (n = 9) over the period 1995–2007 (Fig. 6e). During this season, concentrations of nssSO$_4^{2-}$ and NO$_3^-$ showed the strongest decreasing trends. Moderate changes in pH were observed in the winter due to insignificant changes in nssSO$_4^{2-}$ concentrations, no

changes in NO_3^- concentrations, and decreases in NH_4^+ and Ca^{2+} concentrations. Deposition of H^+ also decreased on a seasonal basis (Fig. 6f), especially in the autumn by -1.4 ± 1.2 eq ha^{-1} yr^{-1} (n = 33, p < 0.1), due to a larger decreasing trend in precipitation.

4. Conclusions

This study compared the chemical composition of atmospheric deposition in France and investigated long-term annual and seasonal evolutions during the period from 1995 to 2007. Data were combined from three different networks, all of which continuously monitor atmospheric deposition chemistry. Despite some methodological differences (*e.g.* type of collector, frequency of sampling and analysis), converging results were found in spatial variations and seasonal patterns. This comparative study has provided evidence that common trends can be detected for inorganic composition in the wet-only and bulk deposition data from the three networks.

Sites with similar chemical characteristics were identified according to the acidity and presence of anthropogenic pollutants or marine and terrigenous ions while the main factors governing temporal and spatial variations in chemical composition and precipitation were highlighted. Climatology, particularly precipitation amount, the origin of air masses (polluted continental, clear oceanic and dusty southern air masses), the presence of aerosols and gaseous compounds as precursors of particles, and anthropogenic and natural emissions strongly influenced the chemical composition of the atmospheric deposition.

The investigations of long-term trends established links between evolutions in the chemical composition of atmospheric deposition and their determinants. Some significant decreases in precipitation were determined on an annual basis. In the summer, precipitation significantly increased in northern France. The same trend analysis was performed on the concentrations and deposition of major components over the 1995–2007 period. The increase in annual pH was homogeneous except for the central western part of France ($+0.3 \pm 0.1$ pH units over 13 years). This significant decrease in acidity was mainly due to the reduction in SO_2 emissions, as evidenced by the decrease in $nssSO_4^{2-}$ concentrations (-115 ± 43 eq ha^{-1} over 13 years), suggesting that changes in the amount of sulphur emitted by European countries have accompanied changes in the chemical composition of atmospheric deposition. This study highlights the lack of any relationship between the reduction in NO_X emissions and the changes in NO_3^- concentrations. Regulations to reduce NH_3 emissions seem to be moderately related to trends in NH_4^+ concentrations. However, a significant decrease was observed in the annual NH_4^+ concentrations in the western, northern and north-eastern parts of France. In addition to the decline in others components, the decrease in base cation deposition resulted in moderate changes in pH values. Decreases in $nssSO_4^{2-}$ and NH_4^+ concentrations on an annual basis were strongly controlled by decreases in the summer. Changes in particle speciation could be partly responsible for these trends. Complementary studies are required to describe those source-receptor links fully by applying multivariate methods to identify the sources of the ionic concentrations observed.

Qualitative and quantitative assessments of atmospheric deposition are essential for understanding regional variations and demonstrating the effectiveness of policies to reduce emissions. They are also very helpful in determining whether ecosystems are being affected by acidification or eutrophication, which could be undertaken using the critical load approach (Nilsson and Grennfelt, 1988; Hettelingh et al., 2007; Moncoulon et al., 2007; Henry and Aherne, 2014). Indeed, long-term trends in sulphur and nitrogen depositions ($NO_3^- + NH_4^+$) could have non-negligible consequences due to their impacts on ecosystems, soil solution chemistry and nutrient pools. Further studies are required to characterise the influence of the observed trends on the estimation of critical loads and their exceedances.

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