

Long-term trends in the chemistry of atmospheric deposition in Northwestern Italy: the role of increasing Saharan dust deposition

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ABSTRACT

The Lake Maggiore watershed is one of the areas most affected by acid deposition in Italy. Decreasing sulfate concentration and increasing pH values of precipitation have been observed in this area in the last 15–20 yr. Besides atmospheric deposition, an important factor controlling water acidification and recovery is the episodic deposition of Saharan calcareous dust, which contributes significantly to alkalinity and base cation deposition. At the sampling site at Pallanza, rain chemistry has been investigated since 1975. The frequency and chemical characteristics of alkaline events (pH > 5.6) and Saharan events in particular (distinguished by an exceptionally high calcium and alkalinity content and by the visible presence of red dust) were evaluated at this site. Saharan events, despite their small contribution to total annual precipitation (3–17%), carry a considerable fraction of the annual total calcium and bicarbonate deposition (up to 70 and 100% respectively). The frequency and intensity of alkaline events affect the acidity/alkalinity budget on an annual basis. Apart from the major effect of sulfate decline, the increasing pH of precipitation recorded at the study site since the 1980s might also be influenced by an increased occurrence and intensity of alkaline events. An increase in the export of Saharan dust from arid regions together with changes in the circulation pattern over the Mediterranean area has been hypothesized as the main causes of this trend.

1. Introduction

Studies performed over the past two decades have demonstrated that large amounts of soil dust are moved by winds, mostly from arid regions. North Africa is one of the largest sources of mineral dust in the world (Prospero, 1995). Dust sources are active all year, especially in summer, when they feed strong pulses across the Mediterranean to Europe. Generation, transport and deposition of Saharan dust over the Mediterranean area depend on the prevailing wind circulation and climatic conditions. The process is highly variable across space and time, first of all because dust outbreaks are related to the occurrence of a southerly flow ahead of synoptic frontal systems which move eastwards across the Mediterranean or originate in the North Sahara and move northeastwards (Bergametti et al., 1987). Saharan dust pulses are also highly dependent on any climatological changes which may occur in the Mediterranean region. The frequency and magnitude of dust storm events can be affected by changes in storm tracks as well as by changes in the vertical stability of the atmosphere and in the precipitation regime. Further modifications

in the pattern of dust deposition are determined by variations in the atmospheric circulation at a regional and local level (Giorgi, 1996).

Several studies have already shown that dust pulses affect the chemical composition of rain in areas which can be reached by these events (Lojze-Pilot et al., 1986; Avila and Rodà, 1991, 2002). There is evidence of long-range dust transport as far as Northern Europe (e.g. Franzén et al., 1994). Calcareous dust, sometimes visible in rain events in Italy, originates in North Africa, and two to three times per year can reach the Alpine region where it is deposited in dry form or dissolved in rain. These so-called “red rains” are characterised by high pH values and exceptionally high calcium contents (Rodà et al., 1992; Le Bolloch and Guerzoni, 1995).

Interannual variations in dust transport from North Africa to the Mediterranean region seem to be well correlated with climatic variability related to the North Atlantic Oscillation (NAO). In particular, the increase of desert dust export recorded since the 1970s is fairly well correlated with the upward trend of the NAO index (Moulin et al., 1997). Also De Angelis and Gaudichet (1991) reported an increase in the number of dust pulses of Saharan origin since the early 1970s based on observations of ice cores from the Mont Blanc summit area.

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Several studies of rain chemistry were performed in Italy in the 1970s and 1980s, with special attention being paid to the acidification processes (Marchetto et al., 1994; Mosello and Marchetto, 1996). The results showed that the highest acidity levels and concentrations of acidifying pollutants (sulfate, nitrate, ammonium) were found in Northwestern Italy (Mosello and Marchetto, 1996). In this area the deposition values were close to those found in the most polluted areas of Europe. In particular, the area within the Lake Maggiore watershed borders to the north of the most densely inhabited part of the Po Plain, which receives the highest sulfur and nitrogen loads in Italy (Mosello and Marchetto, 1996). This is due to the high amount of precipitation (up to 2000 mm yr⁻¹) and to the precipitation in this area, which mostly occurs when the wind blows from the south. Previous studies have dealt with the long-term trends of nitrogen, sulfate and acidity deposition in this region and with the chemical evolution of streams and lakes in the alpine and subalpine area (Mosello et al., 2000; Rogora et al. 2001).

Recognition of the problem of acid deposition on a continental scale and its effects on ecosystems prompted the establishment of several international protocols under the Convention on Long Range Transboundary Air Pollution (CLRTAP) (UN-ECE, 1996). Due to these efforts, there has been a significant improvement in the quality of atmospheric deposition. There has been a large decrease in SO₄²⁻ deposition at many European sites in the last 15–20 yr (Evans et al., 2001), due to reduced emissions of sulfur oxides. As a consequence, the deposition of acidity has also decreased and positive trends of precipitation pH have been recorded in several areas since the 1980s (Evans et al., 2001; Skjelkvåle et al., 2001). Given a sufficient reduction in the deposition of acidifying compounds over a sufficiently long time period, the damaged ecosystems are expected to recover towards their pre-acidified conditions. The degree of reversibility will vary according to the regional characteristics of catchments and regional patterns in reduction of deposition. Recovery in different areas could be more or less marked according to the role played by the so-called confounding factors. These are changes in any environmental factor, other than deposition of sulfur and nitrogen, which affects the biogeochemical system of the catchment and its functioning in determining surface water chemistry. They include meteorological influences, deposition of sea salt and dust, rainfall variation and changes in land use or vegetation (Ferrier et al., 2001). The role and the magnitude of the influence of these factors is currently unknown. Confounding factors that can play a major role in the study area are those related to climate change, such as climate warming, even on a short time scale (years to decades) and extreme climatic events (drought, floods). Furthermore the episodic deposition of Saharan dust can neutralize the acidic input associated with atmospheric deposition (Avila and Rodà, 1991; Psenner, 1999), so accelerating the recovery of ecosystems. This hypothesis was tested in the area of Lake Maggiore using chemical data of precipitation collected at the sampling station at Pallanza since the mid-1970s. This paper

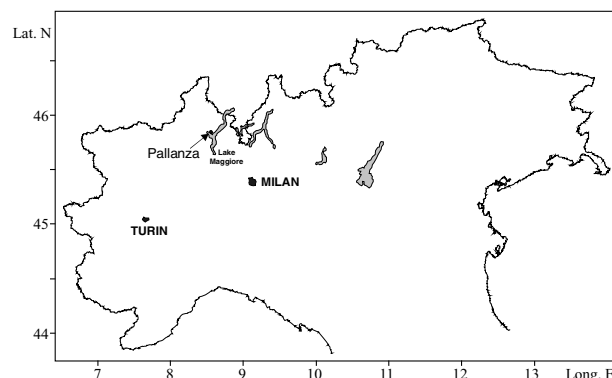


Fig. 1. The location of the atmospheric deposition sampling site at Pallanza in Northern Italy.

aims to show the major variations which have occurred in rain chemistry at this site, focusing on the contribution of Saharan episodes to the annual deposition of alkalinity and calcium. The possible effects of Saharan dust and alkaline deposition in general on the pH value of precipitation and its changes in time are also discussed.

2. Study area and methods

The sampling station at Pallanza (latitude 45°55'N; longitude 8°34'E) is located on the shore of Lake Maggiore (Northwest Italy), in the southern part of the lake watershed, at 208 m above sea level (Fig. 1). Precipitation in this area is mainly determined by warm, moist air masses entering the Po Plain from the Mediterranean and colliding with the Alps. The air rises and cools, producing orographic precipitation which is more intense in the subalpine area, where annual precipitation above 2000 mm is frequent (Carollo et al., 1985). The sources of atmospheric pollutants are mainly located in the Po Valley, south of the Lake Maggiore catchment, creating a pollutant concentration gradient with highest concentrations in the south and gradually decreasing towards the north of the catchment (Della Lucia et al., 1996).

Chemical data for precipitation were collected at Pallanza in 1975 to 1976 and then continuously since 1980 (Table 1). Some changes in sampling frequency and methods were made during

Table 1. Sampling frequencies and methods in use at the atmospheric deposition sampling station at Pallanza since 1975

Period	Sampling frequency	Sampling method
1975–1976	Per event	Bulk
1980–1988	Per event (pH, cond.)	Bulk
1982–1988	Weekly	Bulk
1988–1992	Per event	Bulk
1993–2002	Per event (pH, cond.)	Bulk
1984–1992	Weekly	Wet-only
1993–2002	Per event	Wet-only

the study period. Monitoring has been performed at Pallanza with a bulk collector since the beginning; since 1984 a wet-only sampler has also been used (Table 1). Bulk samplers are constantly open to the atmosphere and collect the sum of wet and dry deposition. Wet-only samplers are only open to the atmosphere when precipitation events occur.

Since 1993 bulk samples collected after each rainfall event have been analysed for only pH and conductivity. The remaining chemical variables were determined on wet-only precipitation samples.

Rain samples were analysed for amount of precipitation and major chemical determinants: pH, conductivity at 20 °C, alkalinity (acidimetric titration, Gran's method), ammonium (spectrophotometry, indophenol blue), base cations (Ca^{2+} , Mg^{2+} , Na^+ , K^+), and strong acid anions (SO_4^{2-} , NO_3^- , Cl^-) (ion chromatography) (Tartari and Mosello, 1997). All the analyses, with the exception of pH and conductivity, were performed on filtered samples (0.45 μm micropore filters). To check the analytical quality for each analysis a comparison between the sum of anions and cations and between measured and calculated conductivity was performed. Further quality assurance measures involved the use of control charts and the analysis of synthetic samples on a regular basis. Participation in several interlaboratory comparisons on rain water analysis allowed a further quality check of the results (e.g. Mosello et al., 1998).

To perform trend analysis on data collected over decades, any new analytical methods were tested for comparability. The methods used for the analysis of pH, conductivity and ammonium were unchanged. In contrast, ion chromatography replaced the methods used for the analysis of sulfate (turbidimetry, until 1984), chloride (ion selective electrode, until 1984), nitrate (spectrophotometry, salicylate until 1986) and base cations (atomic adsorption spectrophotometry, until 1991) (Tartari and Mosello, 1997). After any change in the analytical method, paired analyses were performed to detect possible systematic differences in the results. It emerged that sulfate and chloride concentrations may have been overestimated with the older techniques, particularly at lower concentrations, so that data collected before 1984 were not taken into consideration (Della Lucia et al., 1996).

From the rainy events recorded at Pallanza since 1975, two types were selected and discussed: (i) alkaline events, those with pH above 5.6; and (ii) Saharan episodes, as a subgroup of the alkaline events, distinguished by a high calcium and alkalinity content and by the visible presence of red dust on the funnel wall or on filters.

Alkalinity in rain samples may be derived from different sources; usually it comes from local dust, such as soil dust remobilized by the wind or dust coming from urban/industrial sources. These contributions are usually negligible at the study site. The area surrounding the sampling station at Pallanza is mainly characterized by the presence of low-weathering rocks. Furthermore, the influence of dust coming from local urban activities is low

(Mosello et al., 1988). Dust with a remarkable content of calcium and bicarbonate ions may also be moved by the wind from arid regions at a distance of many kilometres. When major events occur, the dust is partly deposited onto surfaces and partly dissolves in rain, determining exceptional chemical characteristics.

Both a bulk and a wet-only sampler have been used at Pallanza since 1984 (Table 1). A bulk sampler is a continuously open collector, which collects both the wet precipitation and that fraction of dry deposition which sediments gravitationally. A comparison of the chemistry of bulk and wet deposition for the period 1984 to 2002 showed that the differences were very small for pH values and below 10% for ammonium, sulfate, nitrate and sodium concentrations. Differences proved to be slightly higher for calcium, magnesium and alkalinity values (18, 24 and 22% respectively). The same comparison was performed focusing on alkaline events only (weekly samples for the period 1984 to 1988). Even relying on a limited number of samples, the differences between bulk and wet data were less than 20% for all variables.

As bulk precipitation data are available since 1975 to the present day, they may be used to examine the long-term changes in precipitation chemistry at Pallanza. However, in some periods only pH and conductivity were determined on rain samples (Table 1).

Bulk data were used to select alkaline events on the basis of pH value and Saharan events were identified at the first step using the presence of red dust on the funnel wall or on filters as selection criteria. The analyses performed on wet-only samples were used for detailed chemical characterization of the selected Saharan events. The corresponding chemical analyses of wet-only samples were attributed to each of the Saharan events recorded for the period 1993 to 2002. For the earlier period (1984 to 1992) weekly samples were analysed for all the major chemical determinants. When the Saharan event was the only precipitation episode in a week, the analysis of the weekly wet-only sample was considered as a Saharan event. Other Saharan events were not included in the following discussion and calculation of ionic fluxes, as it was impossible to distinguish it from other precipitation episodes of the same week.

After this procedure, the classification of Saharan episodes was refined with respect to the overall chemical analysis associated with each sample, in particular pH values, calcium and alkalinity concentrations. An episode was classified as Saharan only when several indicators confirmed its African origin. If only one or two indicators were present (e.g. high pH value but standard concentrations of alkalinity and calcium compared with the long-term mean values) it was classified simply as an alkaline event.

In most cases meteorological conditions are characterized by the interaction of air masses of different origins, so that rain sampled has scavenged atmospheric components from different sources (Loÿe-Pilot et al., 1986). It may be that some events of African origin do not present the typical chemical features of red rains which require that a wet air mass crosses a dust

cloud during its African trajectory (Avila and Alarcon, 1999). For this reason, only a few events can be definitely classified as of Saharan origin, but many more episodes are probably under the influence of Saharan dust pulses. Several episodes classified here as alkaline may belong to this latter group.

3. Results and discussion

Deposition at the sampling site of Pallanza is moderately acidic and is characterized by unusually high concentrations of nitrogen compounds, among the highest recorded in Europe (Mosello et al., 2000). The amount of precipitation is highly variable at this site. The long-term mean value for the period 1975 to 2002 is 1940 mm, with a minimum value recorded in 1980 (1340 mm) and a maximum in 2002 (3008 mm).

The chemistry of recent wet precipitation at Pallanza is shown in Table 2 as volume weighted mean concentrations of the major variables. Owing to the high interannual variability affecting rain chemistry at this site, the mean values of the last 3 yr (2000 to 2002) were used. The median pH was 4.77, with values ranging from 3.58 to above 7.0. Sulfate and nitrate form the majority of the anions, together accounting for about 40% of the total ionic content. Ammonium is the major cation and secondly calcium (24% and 14% of the ionic content respectively). Altogether, base cations (calcium, magnesium, sodium and potassium) account for almost 23% of the total ionic content. The influence of sea spray is low at this site, owing to the distance from the sea, so chloride and sodium concentrations are low (about $10 \mu\text{eq l}^{-1}$) (Table 2). The mean value of alkalinity was $21 \mu\text{eq l}^{-1}$; but this is strongly affected by the high alkalinity concentration recorded in 2002 ($28 \mu\text{eq l}^{-1}$), which is considerably above the long-term mean for the period 1975 to 2002 ($5 \mu\text{eq l}^{-1}$).

Table 2. Chemistry of wet precipitation at the sampling station of Pallanza in the period 2000 to 2002

	Min.	Max.	Mean	SD
Volume (mm)	2.2	446.3	123.0	83.0
pH	3.58	7.08	4.77 ^a	0.78
Cond. 20 °C ($\mu\text{S cm}^{-1}$)	5.8	210.9	18.7	21.4
H ⁺ ($\mu\text{eq l}^{-1}$)	0	263	15	29
NH ₄ ⁺ ($\mu\text{eq l}^{-1}$)	0	1205	52	117
Ca ²⁺ ($\mu\text{eq l}^{-1}$)	0	221	32	34
Mg ²⁺ ($\mu\text{eq l}^{-1}$)	0	48	4	6
Na ⁺ ($\mu\text{eq l}^{-1}$)	0	143	9	16
K ⁺ ($\mu\text{eq l}^{-1}$)	1	86	3	8
Alkalinity ($\mu\text{eq l}^{-1}$)	0	208	21	33
Cl ⁻ ($\mu\text{eq l}^{-1}$)	1	130	9	15
SO ₄ ²⁻ ($\mu\text{eq l}^{-1}$)	8	300	41	40
NO ₃ ⁻ ($\mu\text{eq l}^{-1}$)	7	685	40	70

Mean values are volume weighted mean concentrations of the 3-yr period.

^aFor pH the median value was used.

The chemistry of precipitation at Pallanza has undergone some changes during the study period, mainly as a consequence of variations in the emissions of anthropogenic pollutants in the last few decades. In particular, data available from the EMEP monitoring programme show a reduction of SO₂ emission in Italy from about 3500 ktonnes yr⁻¹ in the 1980s to less than 1000 ktonnes yr⁻¹ at present (Vestreng, 2001).

The mean annual bulk deposition of the major chemical variables at Pallanza since 1975 is shown in Fig. 2. The data series were tested for trends using the seasonal Kendall test (Hirsch et al., 1982) applied to monthly blocks of data and trend slopes were calculated according to Sen (1968). Sulfate deposition has almost halved at this site since the 1980s, with free acidity decreasing from 90–100 meq m⁻² yr⁻¹ to about 20 meq m⁻² yr⁻¹ and median pH values increasing from 4.3–4.4 to about 5.0. Trends of both sulfate and hydrogen ions proved to be highly significant ($p < 0.001$), with trend slopes of -2.4 and $-1.8 \mu\text{eq l}^{-1} \text{ yr}^{-1}$, respectively. On the other hand, the deposition of inorganic nitrogen did not change during the study period (Fig. 2), and trends both of ammonium and nitrate were not significant ($p > 0.05$). Base cation deposition significantly decreased ($p < 0.001$), with trend slope of $-0.8 \mu\text{eq l}^{-1} \text{ yr}^{-1}$, even though high deposition values were recorded in recent years (about 130 and 170 meq m⁻² yr⁻¹ in 2000 and 2002 respectively). Alkalinity values also increased slightly ($p < 0.01$, trend slope $3.3 \mu\text{eq l}^{-1} \text{ yr}^{-1}$). Similar trends were found at the other study sites in the Lake Maggiore watershed for which long data series are available (Rogora et al., 2001; Barbieri and Pozzi, 2001), and are also confirmed by the data from other sampling stations in Northern Italy (Tait and Thaler, 2000).

The whole data series available for Pallanza was evaluated to determine the occurrence and seasonal frequency of alkaline and Saharan events (Figs 3 and 4). In total, 118 alkaline events have been recorded at Pallanza since 1975. Of these, 49 were classified as Saharan on the basis of their chemical characteristics (Table 3) and the visible presence of red dust. They were characterized by a highly variable precipitation volume (mean value 60 mm; standard deviation 79 mm), as has already been shown in other studies on red rain events in the Mediterranean (Lojze-Pilot et al., 1986; Avila et al., 1998). From a chemical perspective Saharan events are characterized by pH values between 5.9 and 8.0, and elevated values of alkalinity and calcium content ($75 \mu\text{eq l}^{-1}$ and $120 \mu\text{eq l}^{-1}$ on average, respectively) (Table 3), which are markedly higher than the mean values for the period 1975 to 2002 ($3 \mu\text{eq l}^{-1}$ and $30 \mu\text{eq l}^{-1}$, respectively). Other ionic compounds such as sulfate, magnesium, sodium and chloride also usually show high concentrations in these Saharan event samples (Table 3).

The number of Saharan events per year was very irregular and generally ranged between 0 and 4–5. An outstanding number of events (eight) were recorded in 2002 (Fig. 3). These events showed a seasonal pattern, with 31 out of 49 events occurring in

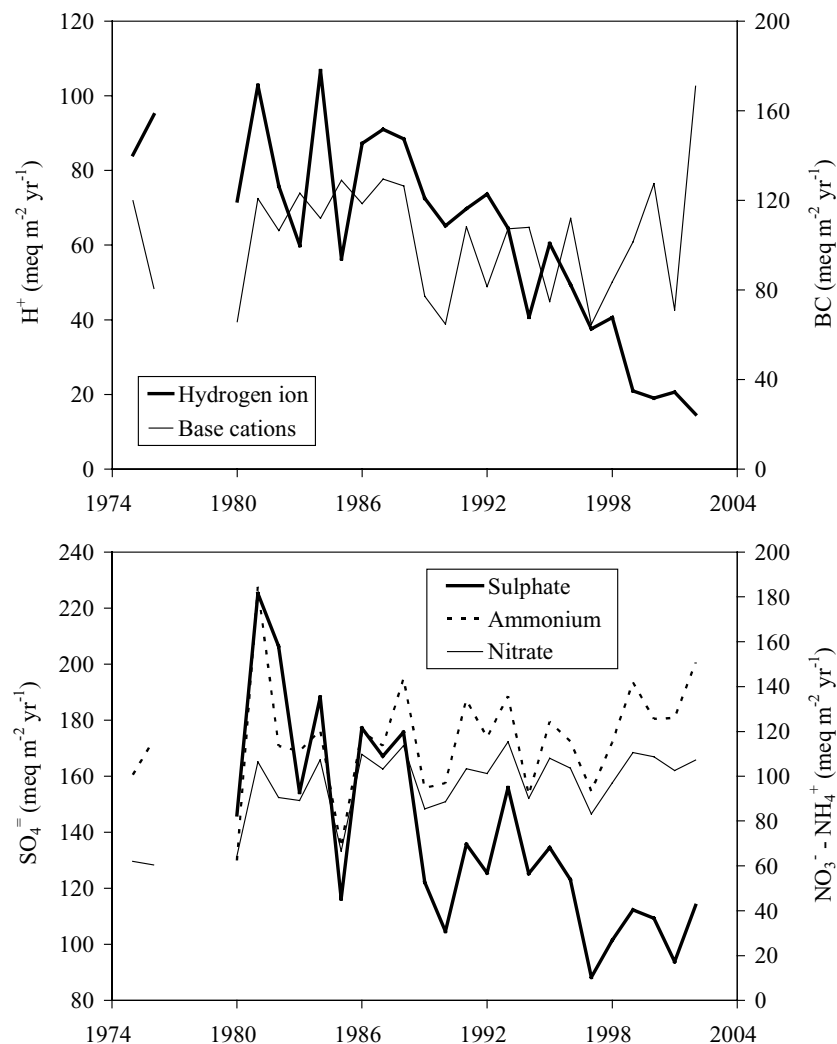


Fig 2. Trends in the annual deposition of the major ions at the sampling station at Pallanza since 1975. Annual values are calculated as the volume weighted mean of monthly bulk data.

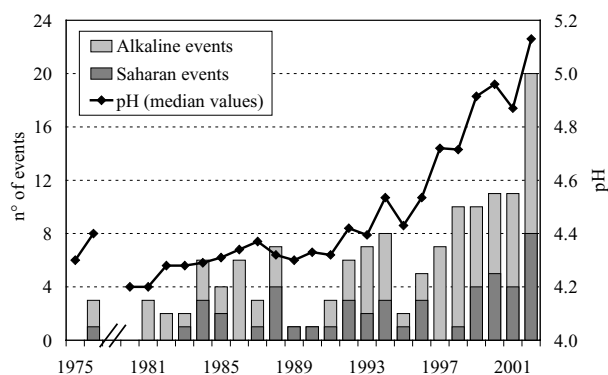


Fig 3. Number of alkaline and Saharan events per year recorded at Pallanza since 1975 and the trend of median pH values.

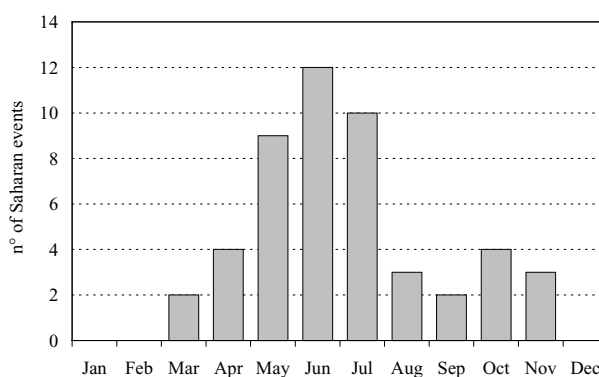


Fig 4. Seasonal pattern of episodic deposition of Saharan dust at Pallanza in the period 1975 to 2002.

late spring to summer (May–July), while no events were recorded in winter (Fig. 4). Le Bolloch and Guerzoni (1995) found a quite different seasonal pattern for the coast of Sardinia (Italy), where peaks of transport events occurred in April–May and again in

October. Maximum inputs of red dust in spring and autumn were also observed in Southern Corsica (Loÿe-Pilot et al., 1986).

The contributions of Saharan events to the total annual fluxes of ionic species dissolved in rain are shown in Table 4. Data

Table 3. Mean concentrations, standard deviation, minimum and maximum values of the major chemical compounds in Saharan events recorded at Pallanza in the period 1984 to 2002 ($n = 49$)

	Min.	Max.	Mean	SD
Volume (mm)	1.4	360.4	163.4	79.8
pH	5.87	8.01	6.71 ^a	0.43
Cond. 20 °C ($\mu\text{S cm}^{-1}$)	13.6	75.6	26.8	16.7
NH_4^+ ($\mu\text{eq l}^{-1}$)	11	392	68	78
Ca^{2+} ($\mu\text{eq l}^{-1}$)	13	664	122	113
Mg^{2+} ($\mu\text{eq l}^{-1}$)	2	178	13	34
Na^+ ($\mu\text{eq l}^{-1}$)	3	112	25	22
K^+ ($\mu\text{eq l}^{-1}$)	1	86	4	13
Alkalinity ($\mu\text{eq l}^{-1}$)	10	320	75	72
Cl^- ($\mu\text{eq l}^{-1}$)	3	66	21	17
SO_4^{2-} ($\mu\text{eq l}^{-1}$)	11	269	73	68
NO_3^- ($\mu\text{eq l}^{-1}$)	0	275	48	56

^aFor pH the median value was used.

prior to 1984 were not considered owing to the use of different methods for the analysis of major anions and cations (Tartari and Mosello, 1997). In some cases, although Saharan events occurred, no chemical analysis was performed owing to the low volume of precipitation. In spite of the low amount of precipitation (3–17% of the annual amount), these events carry from 12% to 76% of the calcium deposition and from 32 to 100% of the alkalinity deposition (Table 4). A weak correlation was found between the number of Saharan events per year and the annual deposition of the major chemical compounds. Some years received

a few events (one or two) but with a high load of calcium and alkalinity. As an example, only one event occurred in 1991, with 32 and 24 $\text{meq m}^{-2} \text{yr}^{-1}$ of calcium and alkalinity deposition, accounting for over 60% and 100% of the annual fluxes.

In the last few years the Saharan events have been more frequent (a total of 21 events in 1999 to 2002) (Fig. 3, Table 4). The events of the years 2000 and 2002 were particularly notable in terms of water volume and contribution to the total ion deposition. The events in 2000 accounted for about 40% and 70% of calcium and alkalinity fluxes respectively. The corresponding values in 2002 rose to 76% and 88% (Table 4). One episode in particular, in mid-October 2000, with a precipitation amount of 340 mm, accounted for 30% and 64% of the deposition of base cations and alkalinity for the whole year.

The median pH values in 2000 (4.96) and 2002 (5.13) were the highest recorded since 1975 (Fig. 3). The general decrease of sulfate deposition affecting Northern Italy has probably played the major role in the increasing trend of pH in rain. A significant negative relation ($r^2 = 0.59$, $p < 0.001$) was found between the annual mean SO_4^{2-} concentration and the median pH values for the period 1984 to 2002. Nevertheless, the highest pH values recorded in recent years are undoubtedly influenced by the increased occurrence and intensity of Saharan events.

Focusing on the last 3 yr, we calculated the mean deposition of free acidity and alkalinity at Pallanza, taking into account all the rain samples (Table 5). Residual acidity was then computed as the difference between free acidity and alkalinity. Intense Saharan events occurred at Pallanza as in the rest of the Lake Maggiore watershed in both 2000 and 2002, with mean alkalinity fluxes

Table 4. Yearly per cent contribution of events containing Saharan dust to the amount of precipitation and to ionic fluxes at the Pallanza sampling station

Year	No of events	% amount	NH_4^+	Ca^{2+}	Mg^{2+}	Na^+	K^+	Alk.	SO_4^{2-}	NO_3^-	Cl^-
1984	3	9	9	55	51	18	22	100	12	10	17
1985	2	11	6	72	13	33	5	–	8	5	6
1986	0	–	–	–	–	–	–	–	–	–	–
1987	1	6	9	47	15	21	12	–	12	7	22
1988	4	8	10	34	22	15	12	100	9	7	15
1989	1	–	–	–	–	–	–	–	–	–	–
1990	1	3	3	24	13	7	4	82	4	3	5
1991	1	12	16	62	30	44	18	100	18	10	34
1992	3	–	–	–	–	–	–	–	–	–	–
1993	2	10	18	40	24	29	15	98	14	17	31
1994	3	13	21	48	27	19	19	91	19	18	17
1995	1	–	–	–	–	–	–	–	–	–	–
1996	3	8	16	34	19	29	17	48	14	12	25
1997	0	–	–	–	–	–	–	–	–	–	–
1998	1	–	–	–	–	–	–	–	–	–	–
1999	4	6	10	21	13	10	10	32	10	10	9
2000	5	17	12	39	25	26	21	70	17	17	24
2001	4	6	4	12	8	7	5	41	5	4	5
2002	8	24	34	76	55	49	52	88	31	28	48

Table 5. Precipitation amount and deposition of acidity and alkalinity (in $\text{meq m}^{-2} \text{ yr}^{-1}$) at the sampling site at Pallanza in the period 2000 to 2002. Residual acidity was computed as the difference between free acidity and alkalinity. Potential acidity was calculated taking the contribution of NH_4^+ deposition into account

	Precipitation volume (mm)	Free acidity (all samples)	Alkalinity (all samples)	Alkalinity (only Saharan events)	Residual acidity	Potential acidity
2000	2560	19	34	23	-15	188
2001	1496	21	7	3	14	189
2002	3008	38	111	97	-73	226

high enough to completely neutralize the inputs of acidity. In contrast, the alkaline deposition in 2001 was unable to buffer the acidity input. Without the contribution of Saharan episodes, the alkalinity flux at Pallanza in 2000 and 2002 would have been of 11 and 14 $\text{meq m}^{-2} \text{ yr}^{-1}$ respectively, which is not enough to buffer the free acidity load (Table 5).

An important source of potential acidity to surface waters is the oxidation of ammonium to nitrate (Van Breemen et al., 1984; Schuurkes, 1986). This process is highly important within the study area, where deposition of ammonium is remarkably high (Barbieri et al., 2003). Taking the ammonium contribution into account, we calculated potential acidity as follows: 1.5 mol H^+ for each mol NH_4^+ oxidized, as a mean value between 1 mol H^+ per mol NH_4^+ (ammonium uptake and H^+ release by algae and macrophytes) and 2 mol H^+ per mol NH_4^+ (microbial oxidation of ammonium to nitrate) (Schuurkes and Mosello, 1988). Based on this the potential acidity calculated for the last 3 yr would be about 190–220 $\text{meq m}^{-2} \text{ yr}^{-1}$ (Table 4), markedly higher than the alkalinity input dissolved in rain.

Nevertheless it should be highlighted that the results shown here refer to analyses carried out on filtered samples and consider only the fraction of alkalinity and calcium dissolved in rain. This did not allow us to consider the contribution from red dust, leading to an overall underestimation of the actual alkaline inputs to terrestrial and aquatic ecosystems.

4. Conclusions

If we consider the different types of rain events recorded at Pallanza since 1975, the number of alkaline episodes has been increasing, in agreement with the trend of pH values.

Saharan events occur irregularly over the whole period, but seem to be more frequent in the last 3–4 yr. Avila and Rodà (2002), studying rain chemistry at a rural site in Northeastern Spain, also reported a recent increase in the occurrence of African rains, finding a significant correlation between the median pH values and the percentage of annual precipitation of African origin (Avila and Rodà, 2002).

Several authors have discussed the implications of episodic depositions of Saharan dust for the acid-neutralizing capacity of the atmosphere (Loÿe-Pilot et al., 1986; Carratala and Bellot, 1998) and for the input of base cations, alkalinity and nutri-

ents to surface water and terrestrial ecosystems (e.g. Avila et al., 1998). Chemical data relating to precipitation collected since the mid-1970s at a sampling site in Northwestern Italy showed that, despite their low amounts of precipitation (3–17% of the annual precipitation volume), Saharan events carried a considerable fraction of the total calcium and alkalinity deposition affecting this study area, and contributed significantly to the buffering of the mineral acidity of precipitation. Evaluating the role of these episodes in the neutralization of acid rain will require further investigation of their relationship with atmospheric circulation patterns.

The effect of alkaline episodes may be particularly important within the study site for areas sensitive to acid deposition such as alpine lakes. Estimating the contribution of dust to the chemical variability of these ecosystems is not easy, owing to the lack of quantitative studies in remote areas (Psenner, 1999). Nevertheless, the frequency and magnitude of dust events and their effects in terms of alkalinity inputs through atmospheric deposition cannot be neglected when dealing with acidification and recovery processes at acid-sensitive sites. The high calcium content of Saharan aerosols as well as the dissolution and release of calcium from the snowpack may be important for biogeochemical cycles involving acid neutralization (De Angelis and Gaudichet, 1991; Delmas et al., 1996).

It is possible for the neutralization of acidity to occur within clouds and rain but also later, after the deposition of alkaline dust on surface waters or in the catchments, where it can be dissolved by subsequent rain events. According to Avila et al. (1998) the concentration of particulate matter in red rains ranges between 0.5 and 330 mg l^{-1} and particulate inputs are a major contributor of phosphorus, calcium, magnesium and potassium within catchments.

Previous studies have demonstrated that several mountain lakes located in the northern part of the Lake Maggiore watershed, both in Italy (Piedmont) and Switzerland (Canton Ticino), are sensitive to acidic inputs from the atmosphere (Marchetto et al., 1994). A chemical recovery has been detected at several sensitive lakes in the last decade (Rogora et al., 2003). While mainly due to decreasing sulfate inputs, the positive trends of pH and alkalinity at these sites might also be influenced by the increasing occurrence of alkaline rain episodes and particularly of Saharan dust deposition.

An increase in the export of Saharan dust and changes in the circulation pattern over the Mediterranean area could be the main causes of the higher occurrence of alkaline rain episodes in recent years. Besides the effects on acid-sensitive lakes, an increase in the atmospheric input of alkalinity could be of environmental concern for terrestrial ecosystems as well. If the current trend is sustained, there might be consequences for mountain floras. Nevertheless, other aspects of global changes such as increase in air temperature, change in precipitation regime and snow-pack dynamics will probably have the major impact on alpine vegetation.

The approach to the problem of acid rain and atmospheric pollution in general at an international level is now at a crucial point. The protocols under the CLRTAP are at present under revision and there is a requirement to assess the efficiency of emission control scenarios in terms of environmental, economic and social benefits. To this end, an assessment of the different factors affecting the chemistry of atmospheric deposition, both as single episodes and in the long term, is of paramount importance. Future changes in dust deposition associated with other global changes such as climate warming and the increasing frequency of stormy events will be a deciding factor in the response of ecosystems to the atmospheric deposition of pollutants.

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