Status and trend of atmospheric deposition chemistry at the CONECOFOR plots, 1998-2005

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Abstract – Ion deposition in the open field and under the canopy was monitored in 13 CONECOFOR plots during 1998-2005. In spite of the remote location of most plots, atmospheric deposition carries considerable amounts of anthropogenic ions (sulphate, nitrate and ammonium). Deposition acidity is buffered by the deposition of base cations, partially due to the long-range transport of Saharan dust. In the study period, sulphate deposition and deposition acidity significantly decreased, because of the decrease in sulphur dioxide emissions in Europe, while nitrate and ammonia deposition did not show a clear temporal pattern.

Key words: *Deposition chemistry, forest sites, acidity, sulphate, nitrogen, time trends.*

Riassunto – Stato e tendenze della chimica delle deposizioni atmosferiche nelle aree CONECOFOR nel periodo 1998-2005. Questo lavoro descrive la deposizione di ioni di origine antropica in 13 aree permanenti della rete. Benché i siti CONECOFOR siano stazioni remote in ambito forestale, la deposizione di solfati, nitrati e ammonio è elevata, ma la loro distribuzione spaziale è differente: nel caso dei solfati, le deposizioni sono minori nelle stazioni di alta quota, mentre la deposizione di ammonio è elevata nella Pianura Padana e quella dei nitrati è relativamente costante in tutto il Paese. La deposizione di ioni alcalini, in parte di origine sahariana, porta ad una notevole riduzione dell'acidità delle deposizioni su tutto il territorio.

Nel periodo di studio si osserva in molte stazioni una diminuzione della deposizione di solfati e di conseguenza dell'acidità delle deposizioni, nonostante una tendenza alla diminuzione della deposizione di ioni alcalini.

Parole chiave: *Chimica delle deposizioni, siti forestali, acidità, solfati, azoto, tendenze temporali.*

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Introduction

Nutrient cycling and soil acidity are important factors influencing forest distribution, growth and health. During the 1980s the pollutant loads from atmospheric deposition were identified as agents which could destabilise forest ecosystems. Studies focused in particular on the effects of the acidity of atmospheric deposition on the functionality of foliar surfaces, the ion exchange between deposition and foliar surfaces, the alteration of ion ratios in the soil, and the load of nutrients, especially nitrogen, reaching the soil.

Trace gases and particulates present in the atmosphere may be deposited through gravity or interception by the receiving surface. The former mechanism is more important for particles deposited directly ("dry deposition") than for those deposited in drops of water ("wet deposition"). However, a portion of wet deposition, referred to as "occult deposition", occurs through interception, for instance, in the case of fog, hoarfrost or dew (Hicks *et al.* 2000).

The quantity of compounds deposited through gravity does not depend on the receiving surface, and may be estimated with a good degree of precision using both continuously open samplers (*bulk samplers*), which however are also affected by locally generated dust, and automatic samplers which open during precipitation *(wet samplers*). In contrast, deposition by interception depends largely on the nature of the receiving surface, so that direct measurement is more complex. In a forest ecosystem, total deposition may be estimated by analyzing deposition collected in the open field, under the crowns (throughfall), and along the trunks of the trees (stemflow). It should be remembered that the chemical composition of atmospheric deposition is changed through contact

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with the crowns and trunks of the trees. To detect the interaction between atmospheric deposition and the tree canopy, the chemical composition of open field bulk deposition is compared to the quality of throughfall water.

Some ions have prevalently natural origin: sodium and chloride, and a component of sulphate, mainly derive from marine aerosol, and their concentrations depend essentially on the distance of the plot from the sea; calcium, magnesium and potassium, on the other hand, are largely terrigenous in origin. Other ions derive mainly from the washout of atmospheric pollutants such as ammonium, an ion produced by the ammonia emitted in agricultural and stock-raising activities, and nitrate and sulphate, ions produced by industrial, domestic and vehicle fuel combustion.

Atmospheric deposition may be acidic as a consequence of atmospheric pollution: nitrogen and sulphur oxides emitted into the atmosphere during fossil fuel combustion are transformed in the atmosphere into nitric and sulphuric acid, respectively. Nitrogen and sulphur emission increased during the twentieth century because of industrial development and traffic increase. From the 1980s, the protocols agreed under the framework of the 1979 Geneva Convention on Long-range Transboundary Air Pollution (UN ECE 1996) led to a substantial decrease in the emission of sulphur and nitrogen oxides into the atmosphere (Figure 1). Ammonium ion deriving from ammonia emitted by agriculture and stock raising is also present in atmospheric deposition, and can produce further acidity directly in the soil during the process of bacterial oxidation (Schuurkes 1986). In most of Italy, the acidity transported annually by atmospheric deposition to forest soils is partially or totally neutralised by episodic deposition of alkalinity deriving from the long-range transport of Saharan dust.

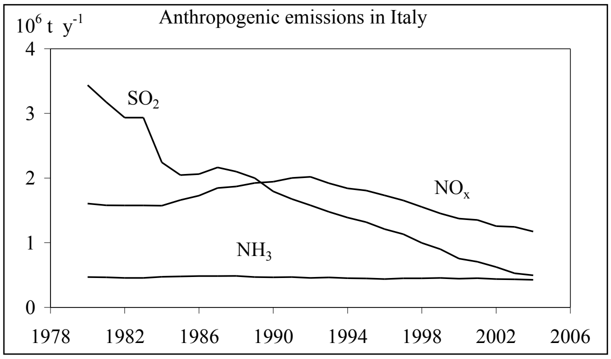

Figure 1 – Trends in emissions in the atmosphere of SO_x, NO_x, NH_3 in Italy (source http://www.emep.int).
Evoluzione temporale delle emissioni di ammoniaca (NH_3) e degli ossidi di zolfo (SO_x) e di azoto (NO_x) in Italia (dati tratti dal sito http://www.emep.int).

Within the CONECOFOR programme, acidity, main ions and nutrient nitrogen inputs from the atmosphere at a maximum of 20 monitoring plots in Italy are analysed.

In this paper we evaluate trends in the amount of precipitation and the concentration of some selected ions in atmospheric deposition reaching the thirteen stations for which analyses were carried out continuously from 1998 to 2005.

This evaluation is designed to detect trends in:

(a) mineral acidity (H^+) of atmospheric deposition and in the input of anthropogenic compounds related to atmospheric pollution, namely sulphate ($SO_4^=$), nitrate (NO_3^-) and ammonium (NH_4^+), in response to emission control enforced by recent legislation;

(b) the amount of precipitation, sea salt contribution (Na^+, Cl^-) and in the basic cation (Ca+Mg) deposition which can buffer the acid input, in response to changes in global and regional atmospheric circulation;

(c) in the canopy response to long-term pollution and its changes, through the analysis of throughfall and runoff water compared to open field deposition.

Methods

Sampling

Open field (OF) depositions were sampled weekly using continuously exposed collectors, comprising a 2-litre graduated polyethylene bottle, with a funnel of 14.5 or 19.5 cm diameter, depending on the mean amount of precipitation to the plot. Three open field collectors were placed in each area, the samples pooled together and an aliquot sent to the laboratory. Snow sampling was carried out in winter 1998 using polyethylene plastic bags placed in PVC tubes, one meter high, with a diameter of 25 cm. Since 1999 the snow samplers have been replaced with a cylindrical PVC container (diameter = 20 cm, height = 80 cm). The snow sample was then melted in a warm room, the volume measured using a graduated cylinder, and the sample bottled for mailing to the laboratory.

For throughfall (TF) sampling, sixteen rain collectors or eight snow collectors similar to those used for the OF were distributed at regular intervals in the plot.

In the same way as for the OF, the samples were pooled together and an aliquot sent to the laboratory.

This paper considers thirteen of the twenty plots: BOL1, CAL1, CAM1, EMI1, EMI2, FRI2, LAZ1, LOM1, PIE1, PIE2, PIE3, TOS1 and TRE1. Bulk open field and throughfall data for the period 1998-2005 were used in the data analysis, with the exception of PIE2 and PIE3, where wet only data were available. The remaining plots were not considered because of gaps in the sampling period, or because they are no longer active in the programme, or because samplings started later than 1998.

Plots PIE2 and PIE3 entered the CONECOFOR programme only in 2003, but wet-only data for the period 1998-2005 are available because of other ongoing research projects. These results were compared with those of the bulk open field of the other permanent plots.

Analysis

The analyses were performed on filtered samples (0.45 µm), except for measurements of pH and conductivity, for which unfiltered samples were used. Major ions (sodium, potassium, magnesium, calcium, sulphate, chloride and nitrate) were analysed by ion chromatography (IC), ammonium and phosphate by spectrophotometry, alkalinity (samples with pH >5.0) by automated Gran titration and total nitrogen by persulphate wet digestion followed by UV spectrophotometric quantification of nitrate. Analyses were performed by the following laboratories: Joint Research Center (Ispra, VA) and CNR-ISE (since 2001) for CAL1, CAM1, EMI1, FRI1, LAZ1 and TRE1; Università di Siena and CNR-ISE (since 2005) for TOS1; CNR Istituto di Ricerca sulle Acque (Brugherio, MI) for LOM1; Agenzia Provinciale per la Protezione dell'Ambiente (Laives, BZ) for BOL1; and CNR-ISE for PIE2 and PIE3.

As sulphate ion derives from both natural (marine) and anthropogenic sources, non-marine sulphate (SO_4*) was calculated on the basis of the $SO_4^{=}/Cl^-$ ratio in sea water (OECD 1979).

Quality control

An analytical quality control programme was set up, involving evaluation of the analytical methods used in the five laboratories taking part in the study, comparison of internal quality controls applied in the laboratories, and the organisation of systematic intercalibration exercises (*e.g.* Mosello *et al.* 1999, 2002b).

Data validation followed the criteria of ion balance and comparison of measured and calculated conductivities (Ulrich and Mosello 2000). Furthermore, comparisons between measured conductivities and sum of cations and anions were performed on the values of each station and each sample type. Deviations from linearity of different sets of values were examined in the light of the completeness of the analyses and considering all the possible causes of errors.

Data pooling

Monthly deposition data were obtained from the sum of the product of weekly concentration by the weekly amount of precipitation. Samples falling between two months were assigned to both, according to the number of sampling days belonging to each month. Monthly pH values were obtained from the volume weighted average concentration of hydrogen ion.

Sampling error

A detailed computation of sampling error for all plots is not available. TF sampling error can be estimated from a study carried out in 1997 on a plot similar to the CONECOFOR plots, located at Ispra (VA), between sites PIE1 and PIE2 (Leyendecker, unpublished), and from a second study carried out in 2006 at site EMI1. In both cases, all sixteen samples were individually analysed on a weekly basis for 15 and 9 weeks, respectively, following the CONECOFOR protocol. The average of the sampling error in the study period was below 10% for all ion concentrations, apart from H^+, and K^+ (both sites), NH_4^+ and NO_3^- (Ispra, only) and Mg^{++} (EMI1, only) for which it ranged between 11 and 19%. This figure represents an upper limit for monthly samples, which integrate 1 to 4 weekly samples.

Statistical analysis

Temporal trends in precipitation chemistry were tested with the Seasonal Kendall Test (SKT) (Hirsch *et al.* 1982) applied to monthly data. SKT has been identified as a suitable method for analysis of water quality data (Loftis and Taylor 1989), and is applied in a number of monitoring programmes, including ICP Waters and ICP Integrated Monitoring (Stoddard *et al.* 1999; Forsius *et al.* 2001). SKT is a refinement of the Mann-Kendall Test, a non-parametric method of trend analysis which is robust with regard to non-normality, missing or censored data (Evans *et al.* 2001). SKT is also robust with respect to seasonality in time series, whereby data are first grouped into either monthly or quarterly mean values (Hirsch *et al.* 1982).

All data pairs within a time series (x_j, x_k, where $j > k$) are assigned a function $\mathrm{sgn}(x_j - x_k)$ with values of +1, 0 or –1 depending on the sign of $x_j - x_k$. These are then summed to give the Mann-Kendall statistic S:

$$(1) \qquad S = \sum_{k=1}^{n-1} \sum_{j=k+1}^{n} \mathrm{sgn}(x_j - x_k)$$

where n is the number of data values. The value of S, together with calculated variance, Var(S), are used to derive a test statistic z, which is positive if the trend is upward and negative if the trend is downward. The magnitude of z is used to estimate trend significance. S and Var(S) are calculated within each seasonal block and summed for all seasons to give full dataset statistics S´ and Var(S´), which are then used to compute z. The estimate of Var(S´) was obtained using a modified procedure presented by HIRSCH and SLACK (1984), which provides a more robust significance test with respect to serial correlation.

Trend magnitudes and slopes were calculated for the monthly deposition of the main ions (H^+, NH_4^+, Ca^{++}+ Mg^{++}, Na^+, Cl^-, $SO_4^=$, NO_3^-) in both bulk and throughfall samples. Significance thresholds of $p < 0.001$, $p < 0.01$, and $p < 0.05$ were applied to trend tests. Trend slopes were calculated according to Sen (1968) as the median of between-year differences in values within each seasonal block.

Results

Quality control and data comparability in time and space

This paper considers only those stations which were run for the whole study period (1998-2005), at least ten months per year. Analytical quality control allowed error detection and repetition of suspect analyses, leading to less than 2% of the analyses showing a difference between measured and calculated conductivity higher than 30%, while for 89% of the analyses the difference was smaller than 15%, which is the target value proposed within the ICP-Forest programme for diluted samples (Ulrich and Mosello 2000).

Data comparability in space and time was assured by uniform sample collection and handling and by the intercomparison exercises for laboratory methods. Apart from the case of TOS1, all the measurements in each plot were made during the seven years of data collection using the same analytical methods.

Present status

The yearly deposition for 2005 of some selected ions, and the amount of precipitation for the thirteen plots, are presented in Table 1, together with the yearly pH obtained form the volume weighted average of hydrogen ion deposition. The amounts of precipitation measured in the bulk open field collectors range between 739 and 2158 mm y^{-1}. The highest value was recorded at CAL1 in the Southern Apennines, the lowest at PIE2, in the Po Plain. Apart from CAL1, all the plots show pH values equal or higher than 5, with a maximum of 5.6 at EMI1 and TRE1: in the past, lower values were recorded for most of the plots. The mean annual fluxes of NH_4^+ and NO_3^- show wide spatial variation, the former ranging from 19 meq m^{-2} y^{-1} (CAM1) to 57 meq m^{-2} y^{-1} (EMI1) and the latter from 20 meq m^{-2} y^{-1} (TRE1 and BOL1) to 57 meq m^{-2} y^{-1} (PIE1). High depositions of SO_4^* (71 meq m^{-2} y^{-1}) were measured at

Table 1 - Annual precipitation (mm) and atmospheric deposition fluxes of some selected ions at the CONECOFOR sites in 2005. SO_4^*: non-marine sulphate.
Precipitazioni annue (in mm) e flussi di deposizione di alcuni ioni nelle stazioni CONECOFOR per il 2005. SO_4^*: solfati corretti per la frazione di origine marina.

2005 *open field*	**mm**	**pH**	**NH_4^+** meq m^{-2} y^{-1}	**NO_3^-** meq m^{-2} y^{-1}	**SO_4^*** meq m^{-2} y^{-1}	**Ca + Mg** meq m^{-2} y^{-1}
BOL1	818	5.5	24	20	13	19
CAL1	2158	4.9	31	40	71	113
CAM1	974	5.2	19	23	28	50
EMI1	935	5.6	57	39	26	33
EMI2	1701	5.2	31	36	33	54
FRI2	1484	5.3	22	24	22	29
LAZ1	1258	5.3	23	27	29	65
LOM1	898	5.3	23	25	18	21
PIE1	1246	5.0	63	57	39	29
PIE2	739	5.4	54	42	31	31
PIE3	907	5.1	27	27	17	20
TOS1	968	5.0	21	28	31	73
TRE1	973	5.6	25	20	13	20
throughfall						
BOL1	604	5.5	11	22	10	36
CAL1	1744	5.3	26	40	102	211
CAM1	776	5.5	16	38	34	99
EMI1	781	5.8	81	63	37	76
EMI2	1246	5.4	31	52	34	85
FRI2	1150	5.8	21	41	29	114
LAZ1	1034	5.4	14	37	31	99
LOM1	744	5.7	23	38	18	45
PIE1	1057	4.9	56	60	35	36
TOS1	735	5.5	14	35	50	157
TRE1	702	5.4	14	18	10	27

Table 2 – Results of the SKT applied to monthly deposition values of the period 1998-2005. Level of significance: p< 0.001 (***), p< 0.01 (**), p <0.05 (*); b: trend slope, meq m^{-2} y^{-2}. SO4*: non-marine sulphate. §: wet only samples.
Risultati del test stagionale di Kendall effettuato sui valori di deposizione mensile per il periodo 1998-2005. Livelli di significatività: < 0.001 (***), p< 0.01 (**), p <0.05 (*); b: pendenza, meq m^{-2} y^{-2}, §: campioni di deposizione umida (wet only).

Open field	mm		H+		NH_4^+		NO_3^-		SO_4^*		Ca+Mg	
	b	p	b	p	b	p	b	p	b	P	b	p
BOL1	-1.8	*	-0.03	**	-0.05	*	-0.04		-1.2	**	-0.06	
CAL1	5.0		0.08	**	0.15	***	0.19	**	-1.3	*	0.06	
CAM1	1.0		0.01		-0.02		-0.14		-3.2	**	-0.92	***
EMI1	2.1		0.00		0.14		0.08		-3.7	***	-0.11	
EMI2	6.3		0.01		0.17	*	-0.14		-3.7	***	-0.29	
FRI2	0.3		-0.03		0.02		0.06		-1.9	**	-0.01	
LAZ1	1.4		0.00		0.04		0.01		-2.4	***	-0.09	
LOM1	-9.5	***	-0.13	***	-0.09	*	-0.17	**	-1.8	***	-0.30	**
PIE1	0.2		-0.11	**	0.10		0.05		-1.7	*	-0.07	
PIE2§	-4.4		-0.09	***	-0.14		-0.23		-2.8	**	-0.06	
PIE3§	-9.5	**	-0.25	***	-0.08	**	-0.20	***	-1.5	***	-0.08	*
TOS1	-1.1		-0.03	**	-0.23	***	0.02		-4.9	***	-0.27	
TRE1	-2.4		0.01	*	-0.03		-0.01		-2.5	***	-0.57	***
Throughfall												
BOL1	-2.0	*	-0.03	***	-0.04	**	-0.07		-3.3	***	0.06	
CAL1	4.6		0.00		0.11	**	0.13	*	-3.0	*	0.31	
CAM1	-3.0		0.01		-0.21	***	-0.14		-2.9		-0.86	*
EMI1	2.0		0.00		0.12		0.16		-5.6	**	-0.11	
EMI2	4.5		-0.00		-0.01		0.01		-5.0	***	-0.03	
FRI2	4.3		-0.10	***	0.03		0.06	*	-3.4	**	0.46	*
LAZ1	0.0		0.00		-0.01		0.04		-2.7	**	-0.04	
LOM1	-7.5		-0.03	***	-0.06	**	-0.09	*	-2.9	***	-0.31	*
PIE1	2.5		-0.03	*	0.02		-0.01		-2.0		-0.15	*
TOS1	-1.4		-0.01	**	-0.23	**	0.19		-7.9	*	-0.89	
TRE1	-2.6	*	0.00		0.00		0.01		-2.6	***	0.33	***

CAL1, while for the other plots the range was from 13 meq m^{-2} y^{-1} (BOL1, TRE1) to 39 (PIE1) meq m^{-2} y^{-1}.

For base cations (Ca, Mg), the sum is reported, ranging from 19 meq m^{-2} y^{-1} at BOL1 to 113 meq m^{-2} y^{-1} at CAL1, with a strong latitudinal gradient. Most of these cations derive from the long range transport of Saharan dust, which is obviously more important at the southernmost sites. Calcium is in general the main cation, followed by sodium, magnesium and potassium. Higher values of magnesium and sodium deposition are registered in the plots closer to the sea, due to the contribution of sea spray. For throughfall chemistry, the fluxes in all the plots are higher than the respective bulk values, with the exception in some cases of ammonium, indicating a possible foliar uptake.

Detected trends

The results of the trend analysis performed on the monthly data of the 13 plots are shown in Table 2. A highly significant negative trend was found for SO_4^* for most of the plots in the case of open field data; the trend slope is negative for all the stations and ranges (in units of meq m^{-2} yr^{-1}) between -4.9 at TOS1 and -1.2 at BOL1. Significant negative trends were also found for H^+ for a lower number of stations, the trend slope varying between -0.25 at PIE3 and 0.08 at CAL1. A significant negative trend was also detected for the sum of Ca and Mg at CAM1, LOM1 and TRE1.

Some stations showed significant trends in precipitation amount. As shown in Figure 2 and 3, detected trends are superimposed on a strong interannual variability, but in the case of sulphate the decrease is clear: its mean decrease from 1998-99 to 2004-05 accounts for 25% and 15% of the 1998-99 sulphate deposition for open field and throughfall samples, respectively. In the case of hydrogen ion, the decrease amounts to 11% and 20%, respectively.

No pattern of significant trends was detected for Na, Cl, K and Mg, either in the open field or in the throughfall samples.

Discussion

In spite of the remote location of many CONECOFOR sites, atmospheric deposition carries high amounts of anthropogenic ions. Apart from some high mountain sites (BOL1, LOM2, PIE3, TRE1, FRI2), bulk sulphate deposition shows values higher than 8 kg S ha^{-1} y^{-1} (25 meq m^{-2} y^{-1}). Ammonia deposition is concentrated in the Po Plain (PIE1, PIE2, EMI1), where it reaches 8-9 kg N ha^{-1} y^{-1} (53-63 mmol m^{-2} y^{-1}), while nitrate deposition is more widespread throughout the country at levels generally ranging between 3 and 6 kg N ha^{-1} y^{-1} (20-42 mmol m^{-2} y^{-1}). These different patterns are related both to the different emission sources and pollutant spread. Ammonia and sulphate are mainly emitted from point sources respectively in agriculture and industry, while nitrate is mainly emitted by diffuse sources, like traffic. On the other hand, ammonia deposition is more related to local sources, while sulphate and nitrate can be transported over long distances. The highest deposition values are found at CAL1 and can be related to the high precipitation amount recorded at this site. Base cation deposition, mainly due to the long-range transport of Saharan dust, is significant at all stations, with a strong latitudinal gradient, allowing the buffering of acid deposition, so that the mean annual acidity is very low at all sites. However, base cation deposition is episodic, and in all sites most of the samples were more acidic.

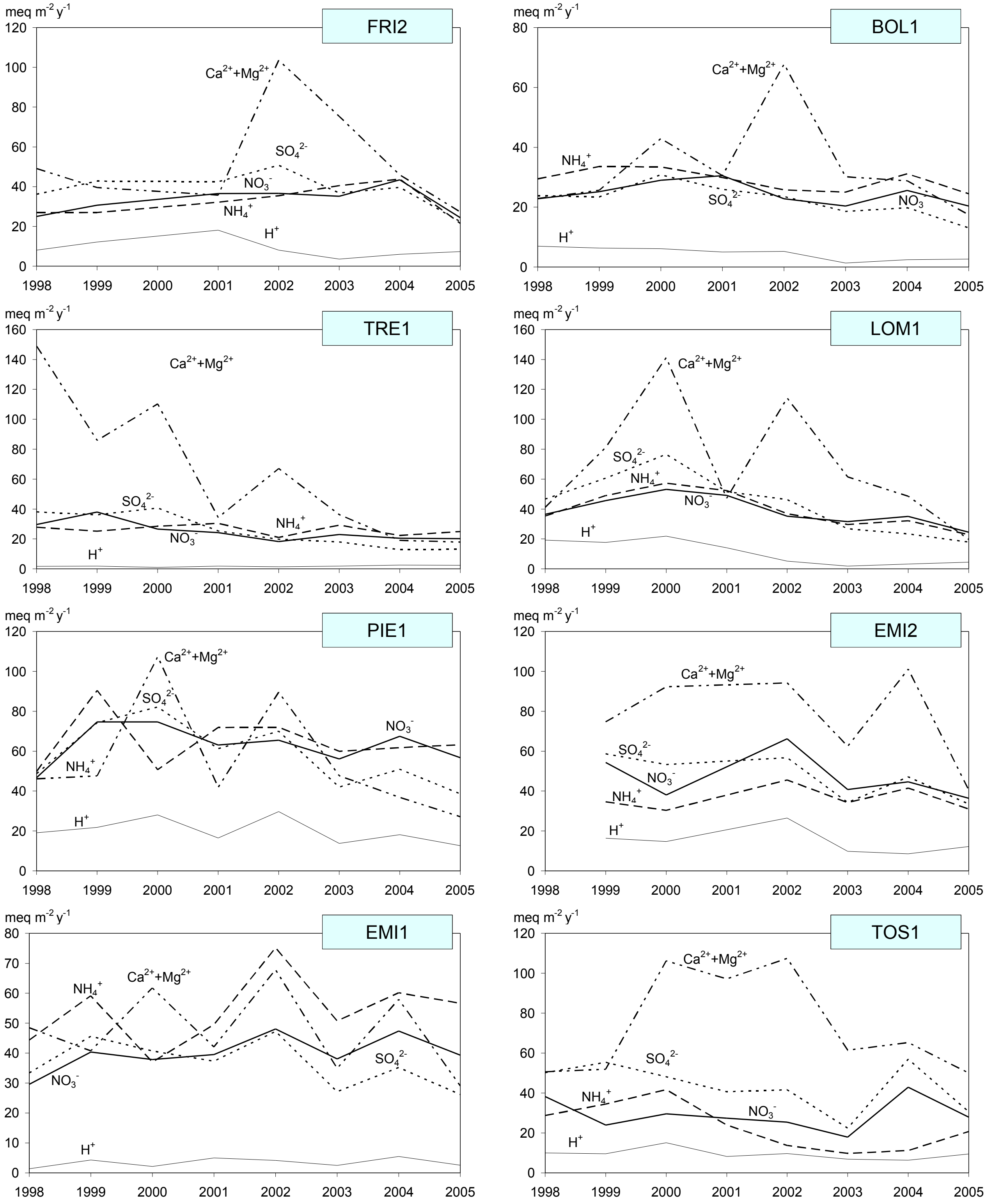

Figure 2 – Open field annual deposition of some selected ions, corrected for sea-salt contribution (in meq m^{-2} y^{-1}).
Deposizione media annua a cielo aperto di alcuni ioni, corretta per il contributo marino (in meq m^{-2} y^{-1}).

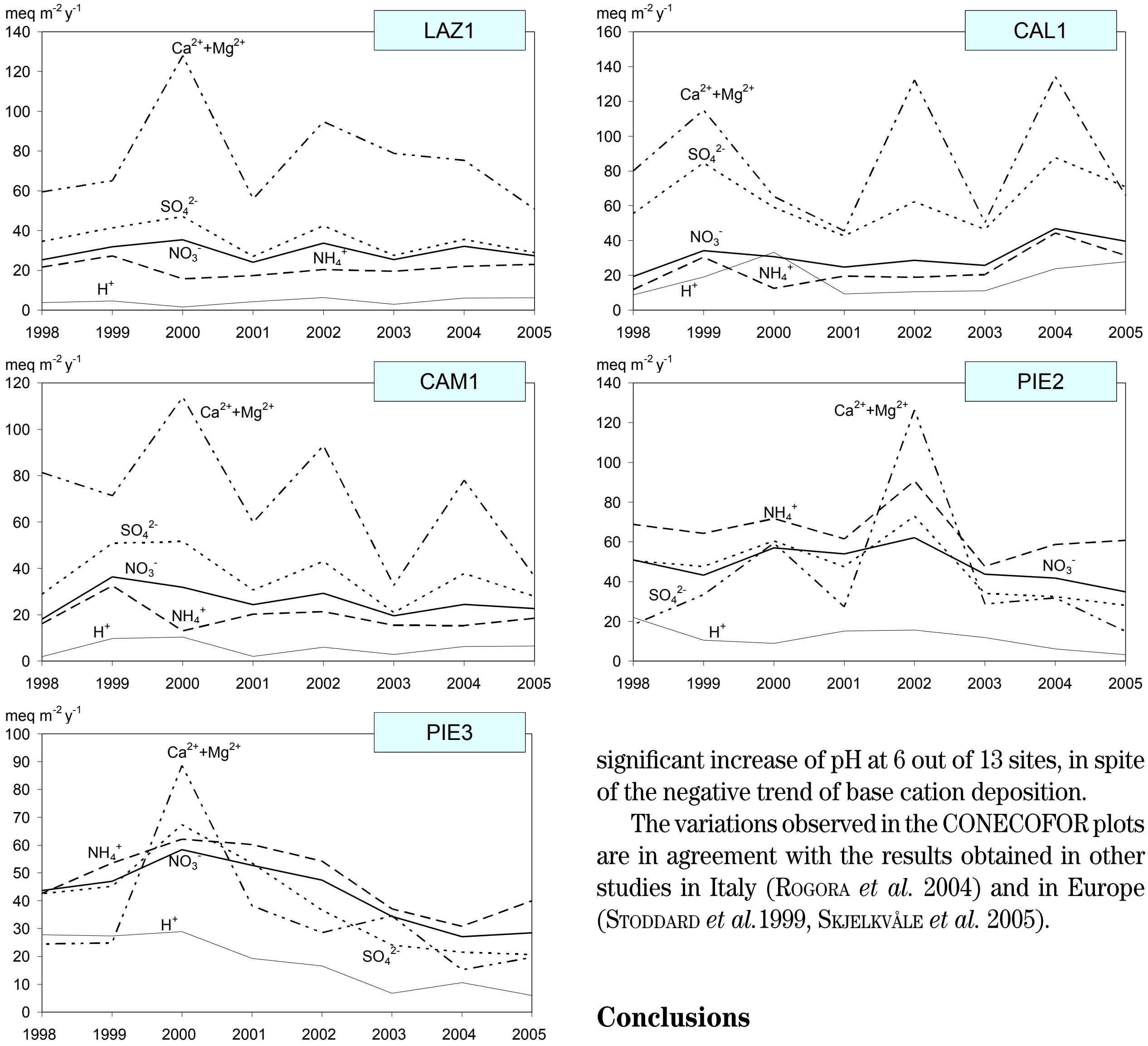

figure 2 (continued)

The interaction with the canopy leads to an increase in sulphate, nitrate and base cations, showing the significant contribution of dry deposition at these sites. In contrast, ammonia is partly retained in the canopy.

Variations in the deposition of sulphate, nitrate and ammonium can be compared to the trends in the emissions of SO_x, NO_x and NH_4 as evaluated by the EMEP (Figure 1). The declining trends of sulphate and acidity in deposition are in agreement with the decreased emissions of SO_x, while the less marked decline in the emissions of NO_x has not yet had an effect on nitrate deposition. Altogether these variations determined a significant increase of pH at 6 out of 13 sites, in spite of the negative trend of base cation deposition.

The variations observed in the CONECOFOR plots are in agreement with the results obtained in other studies in Italy (Rogora *et al.* 2004) and in Europe (Stoddard *et al.* 1999, Skjelkvåle *et al.* 2005).

Conclusions

Atmospheric deposition carries high amounts of sulphate, nitrate and ammonium to all CONECOFOR permanent plots. The lowest values of deposition are in Alpine plots, which however are the most sensitive and fragile from the ecological point of view, while ammonium and sulphate deposition is higher in the Po Plain. On an annual basis the deposition of acidity is low, because of the buffering effect of alkalinity and base cations, enhanced by frequent episodic events of long range transport of calcareous dust from North Africa. Furthermore, this study demonstrated the decreasing trends of both sulphate and acidity, closely related to the decrease in emissions of SO_x into the atmosphere in Italy. On the other hand the deposition of nitrate and ammonium remains high, showing trends only in a small number of plots, furthermore not

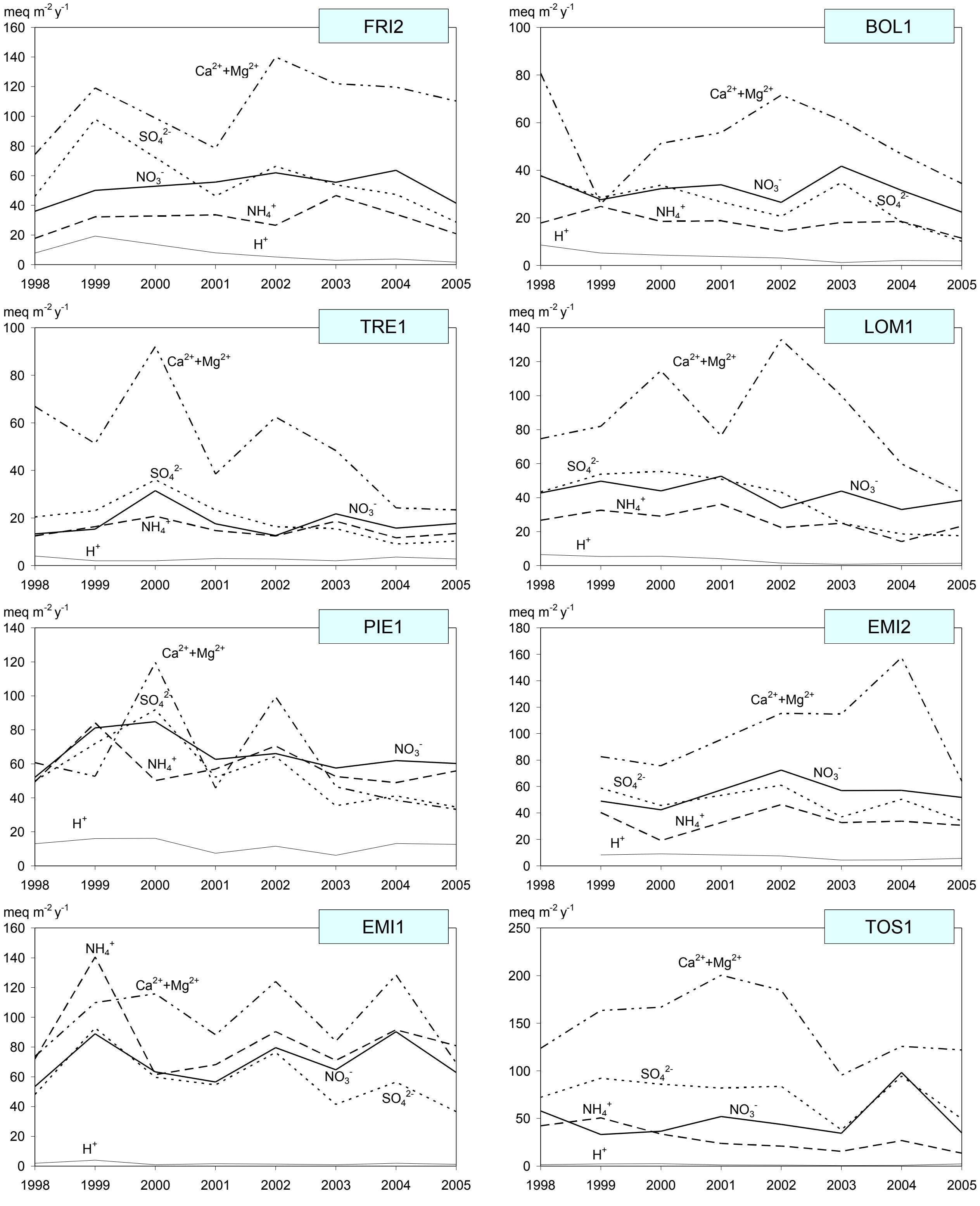

Figure 3 – Throughfall annual deposition of some selected ions, corrected for sea-salt contribution (in meq m^{-2} y^{-1}).
Deposizione media annua sotto chioma di alcuni ioni, corretta per il contributo marino (in meq m^{-2} y^{-1}).

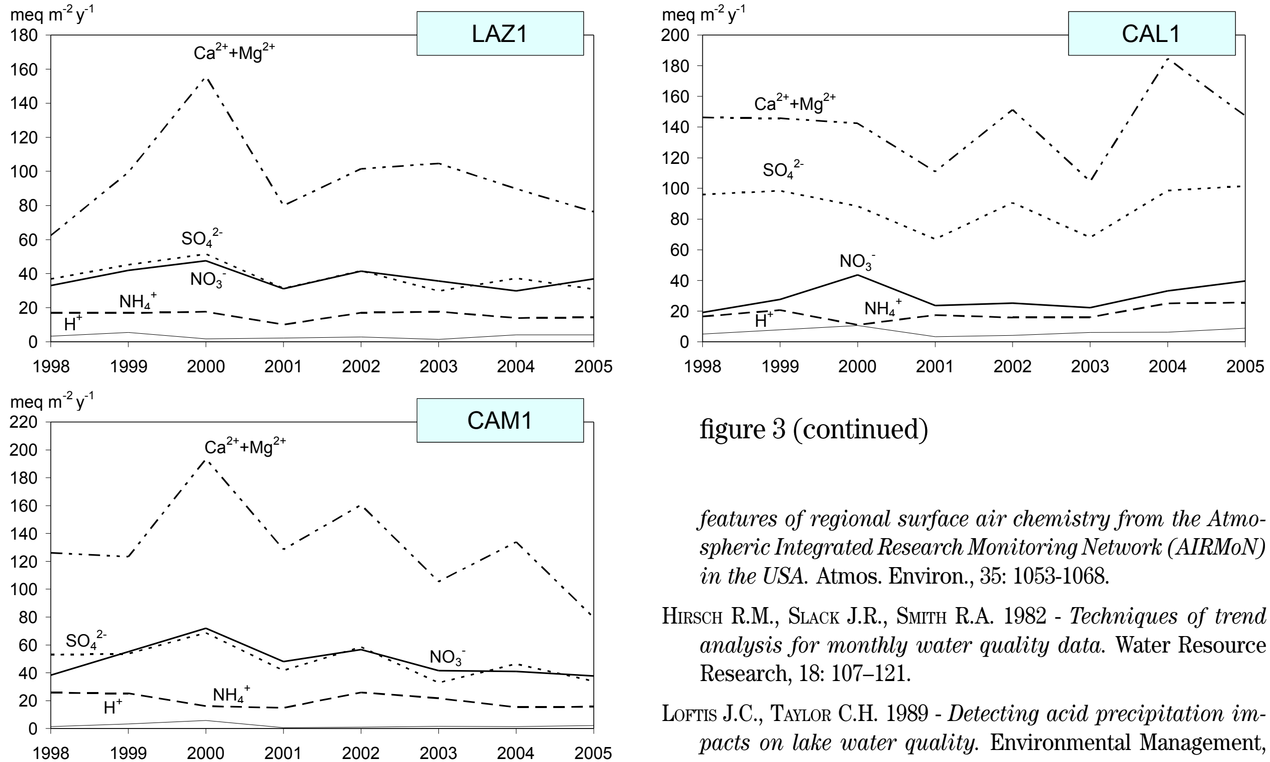

figure 3 (continued)

of the same sign. This is partly in agreement with the pattern of emissions, which is constant for ammonium and only slightly decreasing for nitrate.

Other studies performed in the context of the CONECOFOR project demonstrate the wide exceedance of the actual nutrient N load over the critical load in most of the plots, with nitrate leaching in the surface waters (Mosello *et al.* 2002a; Rogora *et al.* 2003). This confirms that, in the case of Italy, nitrogen deposition remains an important environmental issue. For this reason, significant efforts are still needed to reduce ammonia and nitrogen oxides in the atmosphere, a field on which research and monitoring should be focused in the next few years.

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