The chemistry of atmospheric deposition in Italy in the framework of the National Programme for Forest Ecosystems Control (CONECOFOR)

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ABSTRACT

Under the CONECOFOR programme, allied to the UE and UN-ECE programme on forests (ICP Forests), the chemistry of open field, throughfall and stemflow deposition was measured in 15 permanent plots over a two year period. Characteristics of the plots, sampling methods, treatment and analyses are in strict agreement with those adopted in the European programme. The plots are representative of different geographical conditions, from the Mediterranean area of the southern plots to the Alpine environment. Results show the highest amount of ion deposition related to anthropogenic emissions in the northern (PIE1, VEN1, FRI2) and central (EMI1, TOS1) stations, while most of the central and southern sites show a net flux of alkalinity. The acidity is however buffered by dust and dry deposition present on the canopy, so that the throughfall deposition is always alkaline. Nitrogen, both as ammonium and nitrate, is an important component of precipitation and critical loads are exceeded in most of the areas. This situation is confirmed by analyses of nitrate in runoff, performed in four plots, which show a release from the watershed in all seasons, indicating an overload of nitrogen compared to its possible uptake by vegetation and soil. N saturation is high in the northern and central plots of PIE1 and EMI2, moderate in the central and alpine plots of LAZ1 and FRI2.

Key words: atmospheric deposition chemistry, forest, nitrogen saturation

1. INTRODUCTION

The chemistry of atmospheric deposition and its transformation on contact with vegetation are of great importance in understanding its effects on vegetation. Italian research activity on these topics is co-ordinated by the Ministry for Agriculture and Forest Policy, National Forest Service, (MPA) through the National Integrated Programme for the Control of Forest Ecosystems (CONECOFOR) and forms part of a Pan-European Programme, based on both the European Scheme on the Protection of Forest against Atmospheric Pollution (Council Regulation (EEC) No 3528/86) and the International Co-operative Programme on Assessment and Monitoring of Air Pollution Effects on Forests (ICP Forests) under the Convention of Long-Range Transboundary Air Pollution (UN/ECE) (European Commission, DG VI 1996; De Vries *et al.* 2000).

On the scientific-technical side, the part of the Italian research involving the study of atmospheric depositions is co-ordinated by the Consiglio Nazionale delle Ricerche - Istituto Italiano di Idrobiologia (CNR-III), which is responsible for methodological aspects, collection, validation and elaboration of the results. The Joint Research Centre of Ispra (JRC) co-ordinated analytical quality controls/assurance, and directly performs part of the analytical work. The Research Centre of Brasimone of the Ente Nazionale Energie Alternative (CR-ENEA) is responsible for stemflow sampling.

Methods of sampling, sample treatment and analysis were detailed in a manual distributed to the personnel of the different plot areas and laboratories before the beginning of the project (Allavena *et al.* 1997). This manual was of major importance for quality control, as it provided uniform, detailed methodologies for the various stages of sampling, sample treatment, mailing of samples to the analysing laboratories, and analyses. These techniques are in strict agreement with the "Manual on methods and criteria for harmonised sampling, assessment, monitoring and analysis of the effects of air pollution on forests", prepared for the period 1993-1996 (UN-ECE 1994).

This paper aims to present the methodologies and discuss the results obtained during 1998 and 1999.

2. SAMPLING AND METHODS

2.1. Sampling sites and frequency

Samples for the determination of atmospheric deposition chemistry were taken in 15 permanent plots (Fig. 1). Table 1 reports the codes of each station, which are used in the text to identify the sites. Typical permanent sites for sampling throughfall and stemflow (Fig. 2) are, ideally, located in very large areas which are homogeneous from the point of view of geology and vegetation,
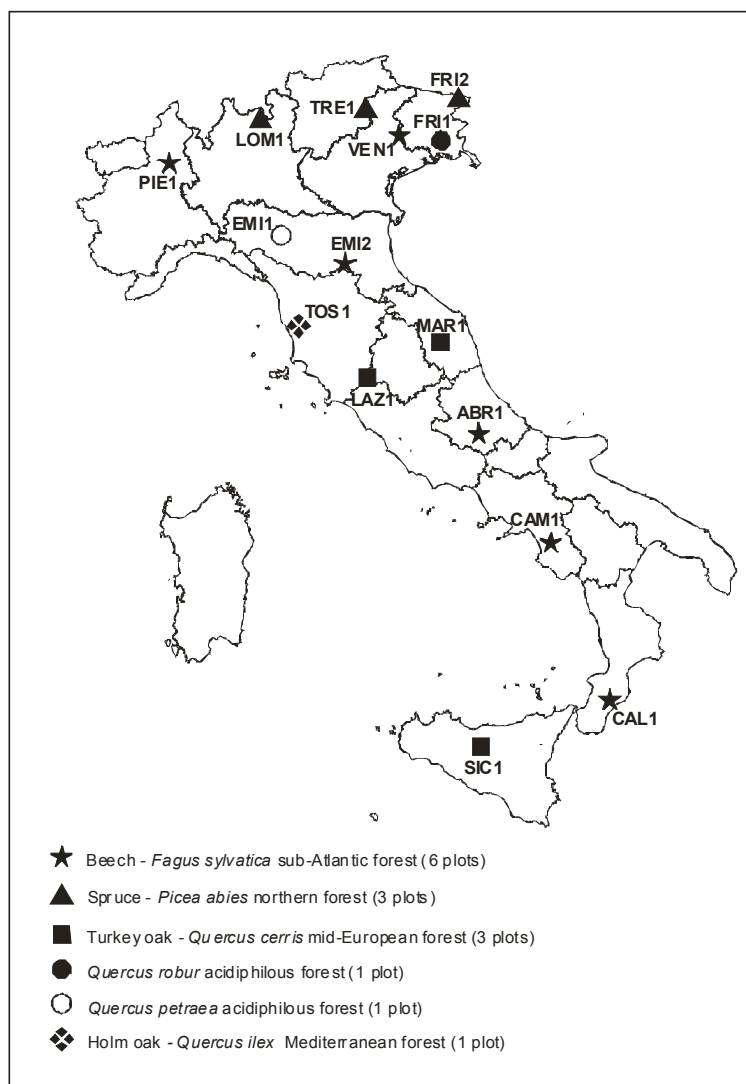
Fig. 1. Location of the permanent plot for atmospheric deposition chemistry with the indication of dominant tree species.

and comprise two plots of 2500 m^2 (squares of 50×50 m). The first of these, called the permanent observation plot, is where the various researches are performed; the second, the reference plot, situated close to the first, is left untouched for the duration of the programme and serves as a comparison to highlight any changes deriving from the impact of the research activity. Each permanent plot (Fig. 3) comprises a central zone, surrounded by a buffer zone approximately 1 metre wide, fenced off to prevent theft or acts of vandalism, and further subdivided into 25 square plots with 10 m long sides.

Samples were collected weekly, on Tuesday morning, with a tolerance interval of 12 hours (from Monday afternoon to Tuesday afternoon), to avoid the start of new precipitation or to allow an on-going event to end. On expiry of the tolerance period on Tuesday afternoon, the samples were collected in any case. When bulk samples were collected, the collecting bottles were changed, even when there was no precipitation, to avoid any accumulation of dust and detritus in the bulk collectors. Volume measurements were performed in the field or, where possible, in a specially equipped room near the study area. The throughfall samples were pooled and the sample aliquots to be sent to the analysing laboratory were then taken.

2.2. Sampling

2.2.1. Bulk (rain or snow), collected in the open field (OF)

Open field depositions were sampled using continuously exposed collectors, comprising a 2-litre graduated polyethylene bottle, with a funnel of 19.5 cm diameter. A polyethylene net in the funnel prevents the collection of coarse debris, insects and leaves. The volume of water collected is 30 ml per millimetre of precipitation. The bottle is inserted into a PVC cylinder of a slightly

Tab. 1. Italian permanent plots for atmospheric deposition chemistry. CFS: Corpo Forestale dello Stato; CR-ENEA: Centro Ricerche Ente Nazionale Energie Alternative; *: Regione; JRC: Joint Research Centre (Ispra); CNR-IRSA: Consiglio Nazionale delle Ricerche - Istituto di Ricerca Sulle Acque (Brugherio); Univ. Siena: Dipartimento Scienze Ambientali Università di Siena. [1]: station not active in the winter period; [2]: research performed in year 1998; [3]: research performed in year 1999.

| Code	Name	Altitude (m a.s.l.)	Dominant species	Throughfall	Open field	Stemflow	Snow	Run off	Wet-only	Managing	Laboratory
				Sampling methods							
ABR1[1]	Selva Piana	1500	*Fagus sylvatica*	X	X	X	X	-	-	CFS	JRC-EI
CAL1	Piano Limina	915	*Fagus sylvatica*	X	X	X	X	-	-	CFS	JRC-EI
CAM1	Serra Nuda	1200	*Fagus sylvatica*	X	X	X[3]	X	-	-	CFS	JRC-EI
EMI1	Carrega	200	*Quercus petraea Quercus cerris*	X	X	X	-	-	X	Natural Park	JRC-EI
EMI2	Brasimone	1000	*Fagus sylvatica*	X	X	X	X	X[2]	-	CR-ENEA	JRC-EI
FRI1	Bosco Boscat	6	*Carpinus betulus Quercus robur*	X[3]	X[3]	-	-	-	-	CFS	JRC-EI
FRI2	Tarvisio	820	*Picea abies*	X	X	X	X	X[2]	X	CFS	JRC-EI
LAZ1	Monte Rufeno	690	*Quercus cerris*	X	X	X	-	X	X	CFS	JRC-EI
LOM1	Val Masino	1190	*Picea abies*	X	X	-	-	-	-	Lombardy*	CNR-IRSA
MAR1	Roti	800	*Quercus cerris*	X	X	-	-	-	-	CFS	JRC-EI
PIE1	Val Sessera	1150	*Fagus sylvatica*	X	X	X[3]	X	X[2]	-	Piedmont*	JRC-EI
SIC1	Ficuzza	940	*Quercus cerris*	X	X	-	-	-	-	Sicily*	JRC-EI
TOS1	Colognole	150	*Quercus ilex*	X	X	X	-	-	-	Tuscany*	Univ. Siena
TRE1	Passo Lavazè	1800	*Picea abies*	X	X	X[3]	X	-	-	Trento*	JRC-EI
VEN1	Pian Cansiglio	1100	*Fagus sylvatica*	X	X	X	X	-	-	CFS	JRC-EI
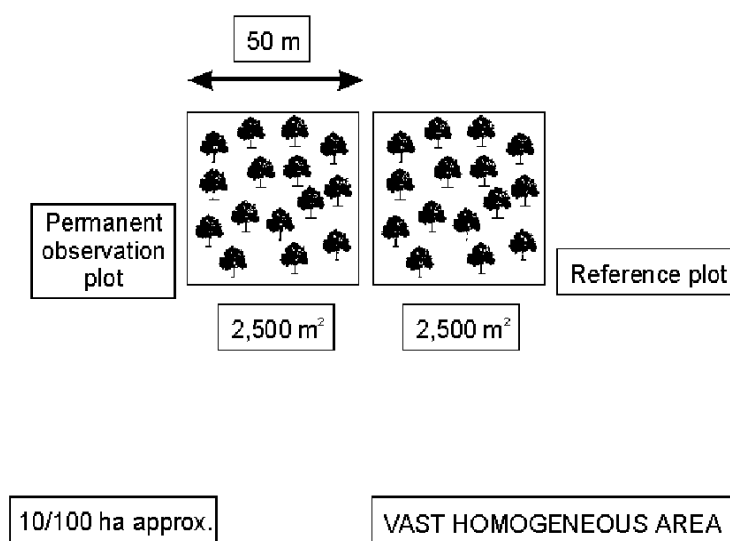
Fig. 2. Diagram of a typical permanent site.

larger diameter, so as to leave an air jacket around the bottle and to shade the bottle. In each area three open field collectors were placed according to the type of sample collected, snow or rain. This meant that a greater number of deposition volume measurements could be obtained, but the chief advantage of using more than one collector is that any samples which were clearly polluted could be discarded, without the loss of the whole sample for the sampling period.

2.2.2. Throughfall (TF)

The collectors were the same as those described for open field sampling. Sixteen collectors were used for TF measurement, distributed evenly over the plot (Fig. 3), as suggested by the ICP Forest Manual (UN-ECE 1994). The precipitation samples were collected weekly, and their volume measured separately and marked on
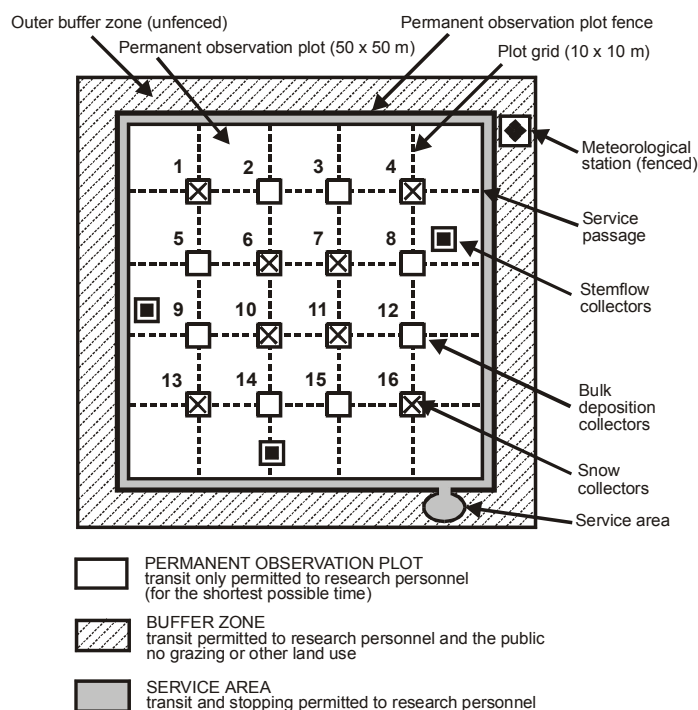
Fig. 3. Diagram of a typical permanent observation plot with the distribution of throughfall ( ) and snow (X) collectors in the permanent observation plot.

the mailing form, to be sent with samples to the analytical laboratories. The precipitation samples were then pooled together and an aliquot sent to the laboratory. Most of the sites were dominated by a single species of tree. In one station (EMI1), where two species were present, the TF samples for each species were kept separate.

2.2.3. Snow

During 1998 snow sampling was carried out weekly using polyethylene plastic bags (diameter = 30 cm) placed in PVC tubes, one meter high, with a diameter of 25 cm; the funnel and bottle collectors used for rainfall are inadequate for the correct collection of snow. As some plastic bags were broken by ice, in 1999 the snow samplers were replaced with a cylindrical PVC container (diameter = 20 cm, height = 80 cm). The snow sample was then melted in a warm environment by exposure to uniform heat. The volume was then measured using a graduated cylinder, and the sample bottled for mailing to the laboratory.

2.2.4. Stemflow (SF)

Stemflow samples were collected on representative trees in the study area taking into account tree age class, diameters and heights. The operators and technicians responsible for this kind of deposition (CR-ENEA) visited each station to select the trees and set up the equipment, and made annual checks that the equipment was in good working order. Three collectors were installed for each station, except in the area (EMI1) with two species,

where six devices were installed, three for each species. Collectors were however placed in only 9 of the 15 active stations; collecting in three other stations (TRE1, CAM1, PIE1) started at the beginning of 1999 (Tab. 1). The stemflow collectors consist of a device for water collection made of ELASTOLEN W300 and are applied directly to the tree stems spiral-wise and fixed with adhesive tape and two nails of such a length as to cause as little as possible damage to the tree. A special connector joins the spiral to a tube through which the water runs into a container of around 120 litres. Stemflow volumes are measured inside the collector with a gauge rod: the volume measured in cm is converted into litres using a conversion table. Samples were obtained by mixing proportional aliquots from the three collectors. Measurements and collection of stemflow water were suspended during the periods of the year when the mean temperature falls below zero.

2.2.5. Runoff

During 1998 runoff water was analysed at four stations (Tab. 1), one of which since April only (EMI2). The watercourse was chosen very close to the permanent observation plot; care was taken to check that the watershed drained had characteristics which were sufficiently uniform, and similar to those of the plot. The sampling point was identified on 1:25,000-scale official Italian topographic maps and marked with a stake. The watercourse was a fairly small stream, but not so small that it was dry for more than 3-4 months a year. The

sample was collected directly with the bottle in which it was sent to the laboratory, care being taken to avoid detritus of large size, such as for example leaf or mud detritus. Sampling was performed weekly, even in the absence of precipitation. The temperature was measured at the same time. During the year 1999 samples were collected only in the station LAZ1.

2.3. Chemical variables considered

The analyses were performed on filtered samples (0.45 μm), except for measurements of pH and conductivity, for which unfiltered samples were used. The samples were filtered in the laboratory.

The variables examined were those of the first level listed in EEC regulation n° 926/93 of 1 April 1993: pH, conductivity, sodium, potassium, magnesium, calcium, ammonium, sulphate, chloride, nitrate, alkalinity (samples with pH >5.0) and total nitrogen (runoff, throughfall and stemflow). Reactive phosphorus was also measured, to reveal any contamination of the samples by bird droppings.

2.4. Analytical quality control

As three different laboratories took part in the chemical analyses (Tab. 1), the data produced had to be perfectly comparable, as well as accurate. To this end a programme of analytical quality control was set up, supervised by the JRC of Ispra, in close collaboration with the CNR-III and the Ministry for Agriculture and Forest Policy. The analytical quality control programme involved:

a) evaluation of the analytical methods used in the laboratories taking part in the study;
b) comparison of internal quality controls applied in the laboratories;
c) organisation of systematic intercalibration exercises.

The different aspects relating to comparability of data and results of intercomparisons were discussed in meetings aimed at the identification and elimination of the causes of errors, involving the people in charge of the different laboratories. The intercomparison exercises were part of a larger project supported by the EU, the Analytical Quality Control and Assessment Studies in the Mediterranean Basin (AQUACON), carried out by the JRC-Ispra in collaboration with CNR-III. These exercises consider samples with characteristics close to both acid deposition and freshwater samples, and yield valuable results for the aims of the CONECOFOR project. The results were published in reports (e.g. Mosello *et al.* 1998, 1999).

2.5. Data validation in the co-ordinating centre

The co-ordinating centre for the studies on atmospheric deposition in the framework of the CONECOFOR project, located in the CNR III, provides validation of the data following the criteria of ion balance and comparison of measured and calculated conductivities (Ulrich & Mosello 2000; Mosello *et al.* 1999). In addition, comparisons between measured conductivities and sum of cations and anions were made on the values of each station and each sample type (bulk, throughfall, stemflow, runoff). Deviations from linearity of different samples were examined in the light of the completeness of the analyses and considering all the possible causes of error.

3. RESULTS

3.1. Open field, throughfall and stemflow deposition chemistry

The amounts of precipitation measured in the open field collectors (Tab. 2) range between 544-582 mm y^{-1} (SIC1) and 1593-2157 mm y^{-1} (LOM1). Values higher than 1000 mm were measured in the stations located in Northern Italy, while the values in the stations in the Apennines and in Southern Italy are more variable and range from 582-544 to 1257-1848 mm y^{-1}.

The mean annual concentrations of ions in bulk OF deposition (Tab. 2) show a wide range of variations, from a minimum of 127 up to 1241 μeq l^{-1} (FRI2 and SIC1, respectively). Most of this variability is due to the marine contribution, as is shown by the wide range of chloride and sodium (8-217 and 7-204 μeq l^{-1}, respectively). The common origin of these ions is well documented by their linear relationship, whose slope is not far from the ratio present in sea water (Fig. 4). A cluster analysis on mean concentrations points out three groups of stations, one of which is comprised of only one station, SIC1. This station shows the highest concentrations of calcium, alkalinity and sulphate. The other two groups are characterised by low (PIE1, LOM1, FRI1, FRI2, EMI1, EMI2, VEN1, TRE1, ABR1) and high (TOS1, MAR1, CAL1, CAM1) concentrations of ions of marine origin. The correction of concentrations for the marine contribution, made on the basis of the ratio of each ion with chloride in sea water (O.E.C.D. 1979), allows an unbiased comparison between concentrations, as sea salt also contributes to sulphate and base cation concentrations (Tab. 2). Alkalinity and calcium are the most important variables in the corrected concentrations. Nitrate and sulphate show the highest concentrations in stations TOS1 and EMI1 (Tab 2). High values of sulphate are also present in the stations CAL1 and SIC1, which may receive a sulphate contribution from the emissions of Mount Etna (Cimino 1984, Jaesche *et al.* 1982; Dongarrà & Varrica 1998), which was active during the sampling period. The ratios between sulphate and nitrate (sea salt corrected values) are between 1.0 and 1.7 in the northern and central plots, and reach their highest values in the southern plots of SIC1 and CAL1 (2.5 and 2.6 respectively). Alkalinity is present in all the stations, generally in mean amounts higher than the mean hydrogen ion concentration, estimated from pH. However, a residual deposition of acidity was detected

Tab. 2. Precipitation amount (mm) and volume weighted mean concentrations for bulk open field deposition for the period 1998-1999. Cond: conductivity at 20 °C; RP: reactive phosphorus; TN: total nitrogen; ON: organic nitrogen, *: concentration corrected for the marine contribution. [1]: calculated from the volume weighted mean concentration of ion H^{+}; [2]: research performed in 1999, only.

		08 FRI2	10 LOM1	17 TRE1	01 ABR1	03 CAL1	04 CAM1	06 EMI2	12 PIE1	20 VEN1	16 TOS1	05 EMI1	07 FRI1[2]	09 LAZ1	11 MAR1	15 SIC1
mm	1998	1335	1593	1048	591	1257	850	845	1252	1203	717	567	-	906	1038	582
mm	1999	1489	2157	1135	567	1848	1428	1433	1995	1530	1006	929	961	1077	1166	544
pH [1]		5.17	5.01	5.78	5.81	5.05	5.29	5.06	4.91	5.2	4.95	5.45	4.82	5.38	5.44	4.89
Cond.	µS cm^{-1}	9.8	11.3	11.8	21.7	28.9	25	19.6	15.2	14.8	32.7	18.6	20.6	22.2	28.7	69
H$^+$	µeq l^{-1}	7	10	2	2	9	5	9	12	6	11	4	15	4	4	13
NH$_4^+$	µeq l^{-1}	18	22	32	25	14	21	26	43	34	37	65	40	24	45	22
Ca^{++}	µeq l^{-1}	23	30	41	105	52	62	54	25	47	59	46	36	59	61	309
Mg^{++}	µeq l^{-1}	7	4	26	15	37	29	18	5	10	33	13	13	25	30	68
Na$^+$	µeq l^{-1}	7	7	9	41	107	98	49	9	12	204	27	36	81	112	199
K$^+$	µeq l^{-1}	3	2	7	8	28	8	9	4	5	16	6	6	7	8	23
Alk.	µeq l^{-1}	8	16	34	77	38	31	25	6	29	43	21	9	24	39	235
SO$_4^=$	µeq l^{-1}	27	29	28	40	57	46	45	39	38	76	52	52	47	47	117
NO$_3^-$	µeq l^{-1}	19	22	20	32	17	24	33	37	28	36	44	40	28	30	38
Cl$^-$	µeq l^{-1}	8	7	10	41	114	106	48	9	13	140	27	39	89	109	217
Σ cat.	µeq l^{-1}	66	76	116	197	247	224	163	99	115	360	161	146	201	259	635
Σ an.	µeq l^{-1}	61	74	92	190	226	207	152	91	108	294	144	140	189	224	606
RP	µg l^{-1}	3	10	104	17	45	14	10	11	5	-	11	17	7	19	39
ON	µM	8	14	19	16	18	15	5	8	12	-	14	10	13	13	37
TN	µM	45	58	71	74	48	60	63	88	75	-	124	90	66	87	97
Ca*	µeq l^{-1}	23	30	41	104	48	58	52	25	47	54	45	35	55	57	301
Mg*	µeq l^{-1}	6	3	24	7	15	9	8	4	8	5	8	5	7	8	25
Na*	µeq l^{-1}	1	1	0	6	9	7	7	1	1	84	3	2	5	18	13
K*	µeq l^{-1}	3	2	6	8	26	6	8	4	4	13	5	5	6	6	19
SO$_4$*	µeq l^{-1}	26	29	26	35	45	35	40	38	36	61	49	48	38	36	95

in two sites (PIE1 and FRI1). Total nitrogen is mainly made up of ammonium and nitrate; the amount of organic nitrogen, calculated from the difference with inorganic nitrogen, is between 5-37 µM, i.e. 8-38% of the total (average 20%). Reactive phosphorus mean concentrations are in most cases lower than 20 µg P l^{-1}, reaching a value of 84 µg P l^{-1} in the southern plot, CAL1.
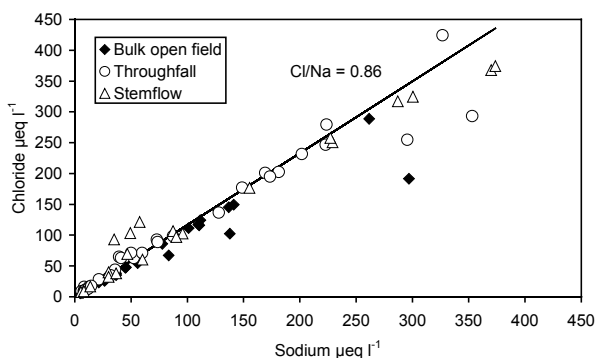

Fig. 4. Relationship between sodium and chloride concentrations in the different samplings in relation to sea water ratio.

Throughfall concentrations in all the stations (Tab. 3) are higher than the respective bulk values; the increase involves alkalinity and the main ions, with the exception of nitrate and ammonium, which in several stations are lower in TF, indicating canopy uptake. However, total nitrogen concentration in TF is always higher than in the open field, indicating a net release of organic nitrogen. In fact, ON constitutes from 13 to 50% of TN, with a mean of 31%. pH values are in the range 4.9-5.8; these values, compared with the range of alkalinity (6-213 µeq l^{-1}), mean that there is a net deposition of alkalinity in all the stations, with the exception of PIE1 (beech stand), with the same values of alkalinity and acidity, and FRI2 (*Picea abies*) where there is residual acidity of 6 µeq l^{-1}. Chloride (11-351 µeq l^{-1}) and sodium (9-318 µeq l^{-1}) show values slightly higher than in bulk deposition, although the ratio Na/Cl remains very close to the marine value (Fig. 4). Potassium shows a more substantial increase: it is present in concentrations of 2-28 µeq l^{-1} in bulk open field deposition, while its values range from 21 to 179 µeq l^{-1} in TF. The increase of reactive phosphorus concentration is also marked, with a range of below 8 to 364 µg P l^{-1}. The correction for sea salt contribution (Tab. 3) shows that most of the sodium is of marine origin, while relatively high concentrations of potassium and magnesium are still present, due to leakage from leaves. Stemflow concentrations (Tab. 4) show significant differences from those of OF and TF deposition, and vary greatly according to the tree species. A general pattern in all the stations is the relevant imbalance of cations and anions, the former much higher than the latter, indicating a considerable presence of organic acids.

Tab. 3. Precipitation amount (mm) and volume weighted mean concentrations for throughfall deposition in the period 1998-1999. Cond.: conductivity at 20 °C; RP: reactive phosphorus; TN: total nitrogen; ON: organic nitrogen; *: concentration corrected for the marine contribution; *Qc*: *Quercus cerris*; *Qr*: *Quercus robur*. [1]: calculated from the volume weighted mean concentration of ion H^{+}; [2]: research performed in 1999, only.

		08 FRI2	10 LOM1	17 TRE1	01 ABR1	03 CAL1	04 CAM1	06 EMI2	12 PIE1	20 VEN1	16 TOS1	05 EMI1*Qr*	07 FRI1[2]	05 EMI1*Qc*	09 LAZ1	11 MAR1	15 SIC1
mm	1998	1047	1303	864	818	1146	937	584	1280	1508	529	525	-	507	804	859	621
mm	1999	1162	1738	857	687	1223	1092	1099	1837	1562	812	792	744	1224	930	1006	601
pH [1]		4.91	5.41	5.45	5.64	5.26	5.64	5.25	5.03	5.3	5.58	5.44	5.6	5.48	5.3	5.66	5.75
Cond.	µS cm⁻¹	24.3	13.3	14.5	36.6	49.1	49.9	31.9	17	16.2	71.7	43.2	45	37	34.4	44.9	87.5
H^+	µeq l⁻¹	12	4	4	2	5	2	6	9	5	3	4	3	3	5	2	2
NH_4^+	µeq l⁻¹	23	20	17	48	16	25	36	43	33	69	149	53	123	19	18	46
Ca^{++}	µeq l⁻¹	63	42	46	109	98	104	70	30	39	121	105	146	79	78	112	271
Mg^{++}	µeq l⁻¹	30	12	26	43	73	70	37	9	15	156	47	83	37	47	53	136
Na^+	µeq l⁻¹	15	9	9	67	175	196	75	10	12	318	37	50	35	114	168	274
K^+	µeq l⁻¹	43	37	28	83	90	64	56	21	29	114	71	109	61	48	68	179
Alk.	µeq l⁻¹	6	15	28	106	57	72	50	9	23	141	99	118	72	27	68	213
$SO_4^=$	µeq l⁻¹	68	33	27	46	103	75	64	40	42	150	90	96	86	61	65	137
NO_3^-	µeq l⁻¹	39	30	17	31	20	46	54	43	32	68	82	53	82	43	44	27
Cl^-	µeq l⁻¹	23	11	12	83	202	219	86	11	14	270	52	71	43	136	188	351
Σ cat.	µeq l⁻¹	186	123	129	353	457	462	281	123	133	781	413	444	338	311	421	908
Σ an.	µeq l⁻¹	136	89	83	265	382	412	254	104	110	629	323	339	284	268	365	727
RP	µg l⁻¹	12	49	27	56	84	23	17	9	36	-	21	13	21	8	19	364
ON	µM	34	26	25	70	36	29	21	13	19	-	34	48	33	26	31	65
TN	µM	96	76	59	149	72	100	112	99	83	-	264	154	238	88	93	137
Ca*	µeq l⁻¹	62	42	46	106	90	96	67	30	39	111	103	144	78	73	105	258
Mg*	µeq l⁻¹	26	10	23	27	33	27	20	6	13	103	37	69	28	21	16	68
Na*	µeq l⁻¹	0	0	0	0	4	8	1	1	0	87	0	0	0	0	7	0
K*	µeq l⁻¹	42	36	28	81	86	60	55	21	29	109	70	107	61	45	64	172
SO4*	µeq l⁻¹	65	32	25	37	82	53	55	39	40	123	85	89	81	47	46	100

Tab. 4. Precipitation amount (mm) and volume weighted mean concentrations for stemflow deposition in the period 1998-1999. Cond.: conductivity at 20 °C; RP: reactive phosphorus; TN: total nitrogen; ON: organic nitrogen; * concentration corrected for the marine contribution; Qc: *Quercus cerris*; Qr: *Quercus robur*. [1]: calculated from the volume weighted mean concentration of ion H^{+}; [2]: station not active in winter; [3]: research performed in 1999, only.

		08 FRI2	17 TRE1[3]	01 ABR1[2]	03 CAL1	04 CAM1[3]	06 EMI2	12 PIE1[3]	20 VEN1	16 TOS1	05 EMI1*Qr*	05 EMI1*Qc*	09 LAZ1
mm	1998	3	-	22	16	-	30	-	21	24	27	20	102
mm	1999	3	0.17	26	17	56	115	206	33	34	44	27	104
pH [1]		4.17	4.07	6.16	5.55	5.24	5.43	5.48	5.67	5.45	5.82	5.29	5.15
Cond.	µS cm⁻¹	107	158	23.7	56.5	64.9	29.1	16.4	13.1	89.5	46.4	53.3	55.3
H^+	µeq l⁻¹	68	86	1	3	6	4	3	2	4	2	5	7
NH_4^+	µeq l⁻¹	30	25	8	5	18	34	46	11	13	144	235	14
Ca^{++}	µeq l⁻¹	276	595	68	87	98	54	20	36	193	87	47	97
Mg^{++}	µeq l⁻¹	129	212	30	72	92	26	7	10	182	28	24	71
Na^+	µeq l⁻¹	42	58	72	228	370	91	8	11	343	30	41	222
K^+	µeq l⁻¹	306	708	68	137	53	63	52	51	252	168	136	110
Alk.	µeq l⁻¹	1	0	43	19	20	22	15	21	91	76	40	13
$SO_4^=$	µeq l⁻¹	343	483	39	147	96	71	45	35	229	96	113	94
NO_3^-	µeq l⁻¹	39	4	19	2	45	51	47	11	52	84	117	65
Cl^-	µeq l⁻¹	98	122	81	254	368	98	9	13	354	35	52	248
Σ cat.	µeq l⁻¹	851	1683	246	533	636	272	136	122	987	459	489	520
Σ an.	µeq l⁻¹	481	609	182	422	529	242	117	80	726	292	321	419
RP	µg l⁻¹	15	55	12	23	12	10	55	48	-	8	6	6
ON	µM	174	308	36	45	25	11	13	33	-	53	57	49
TN	µM	243	338	63	52	88	97	107	55	-	282	410	128
Ca*	µeq l⁻¹	272	591	65	78	84	50	19	36	180	85	45	87
Mg*	µeq l⁻¹	110	188	14	22	19	7	5	8	113	22	14	23
Na*	µeq l⁻¹	0	0	3	10	54	7	0	0	40	0	0	9
K*	µeq l⁻¹	304	705	66	132	46	61	52	51	246	167	135	105
SO4*	µeq l⁻¹	332	470	30	121	58	61	44	33	193	93	107	68

Tab. 5. Mean concentrations of ions in runoff in 1998. Cond.: conductivity at 20 °C; RP: reactive phosphorus; TN: total nitrogen; ON: organic nitrogen; *: concentration corrected for the marine contribution.

		06 EMI2	08 FRI2	09 LAZ1	12 PIE1
pH		8	8.2	8.2	7.6
Cond.	$\mu S\ cm^{-1}$	220	327	576	81
H^+	$\mu eq\ l^{-1}$	0	0	0	0
NH_4^+	$\mu eq\ l^{-1}$	2	4	5	3
Ca^{++}	$\mu eq\ l^{-1}$	1704	2765	4472	411
Mg^{++}	$\mu eq\ l^{-1}$	628	1060	1419	321
Na^+	$\mu eq\ l^{-1}$	148	57	988	56
K^+	$\mu eq\ l^{-1}$	21	14	49	7
Alc.	$\mu eq\ l^{-1}$	1883	3612	5160	765
$SO_4^=$	$\mu eq\ l^{-1}$	356	130	677	24
NO_3^-	$\mu eq\ l^{-1}$	24	6	11	46
Cl^-	$\mu eq\ l^{-1}$	119	41	805	14
Σ Cat.	$\mu eq\ l^{-1}$	2503	3902	6933	799
Σ An.	$\mu eq\ l^{-1}$	2382	3789	6653	850
RP	$\mu g\ l^{-1}$	4	3	10	4
ON	μM	13	6	21	7
TN	μM	39	16	37	56
Ca*	$\mu eq\ l^{-1}$	1700	2764	4443	411
Mg*	$\mu eq\ l^{-1}$	604	1052	1260	318
Na*	$\mu eq\ l^{-1}$	47	22	297	44
K*	$\mu eq\ l^{-1}$	19	13	34	7
SO_4*	$\mu eq\ l^{-1}$	344	125	594	23

The ion difference ranges between 8 and 48% of the cation concentrations, with a median value of 21%. The highest ion concentrations were measured in stemflow in Picea abies (TRE1 and FRI2), with values which are 10-15 times higher than OF bulk deposition and 5-10 times higher than TF. These stations were also the ones where the lowest pH values were recorded (4.1 and 4.2, respectively), with high values of sulphate and ammonium. The lowest concentrations in stemflow were found in *Fagus sylvatica* (ABR1, CAL1, EMI2, VEN1, PIE1) plots with values close to those of TF. Intermediate between these two cases are the stemflow concentrations on *Quercus robur* and *Quercus cerris*, which are about twice those of TF. No sodium uptake from the vegetation is evident in the case of stemflow either; the Na/Cl ratio was close to that of sea water (Fig. 4). The concentrations of organic nitrogen and potassium show a further increase if compared to OF and TF deposition.

3.2. Chemistry of runoff water

The waters of the streams sampled close to the permanent observation plots show high solute and alkalinity values, indicating high soil weathering rates (Tab. 5). Alkalinity values range from 765 $\mu eq\ l^{-1}$ in plot PIE1 to as much as 5160 $\mu eq\ l^{-1}$ in plot LAZ1, where the soil is formed of calcareous clay. Major cations are calcium and magnesium, followed by sodium. Chloride concentrations are very high in LAZ1 (805 $\mu eq\ l^{-1}$), while the lowest mean concentration is measured in PIE1 (14 μeq l^{-1}). The low concentrations of reactive phosphorus indicate, as expected, the absence of fertiliser pollution. As regards nitrogen compounds, ammonium is present in

concentrations below 5 $\mu eq\ l^{-1}$, while nitrate shows mean annual values ranging from 6 to 46 $\mu eq\ l^{-1}$ respectively in the plots FRI2 and PIE1. The monthly mean concentrations, obtained from the weekly measurements (Fig. 5), show increasing values from the plots LAZ1 and FRI2 (below 20 $\mu eq\ l^{-1}$) to EMI2 (between 20 and 30 $\mu eq\ l^{-1}$) to PIE1 (between 30 and 67 $\mu eq\ l^{-1}$). The concentrations of total nitrogen are three times higher than nitrate in FRI2 and LAZ1, while the ratio is 30 and 60% in the case of PIE1 and EMI2.
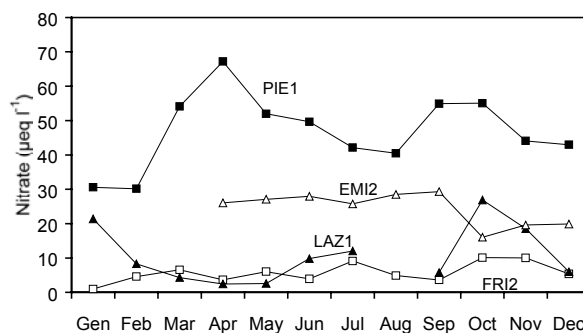

Fig. 5. Mean monthly concentrations of nitrate ($\mu eq\ l^{-1}$) in stream water measured in four station during the year 1998.

4. DISCUSSION

4.1. Validation of results

The ion balance check proved to be reliable in the case of open field bulk deposition and the running waters, but it was not successful with TF and SF deposition, because of the high content of undetermined or-

ganic acids, which systematically resulted in higher concentrations of cations vs anions (Fig. 6, upper). The second check, based on the comparison between measured and calculated conductivity, proved to be reliable for the four types of sample considered (Fig. 6b). The contribution to conductivity of organic compounds is generally poor, and is important only for compounds with low molecular weight. Analyses not passing the test were repeated and, if confirmed, the data were in any case accepted.
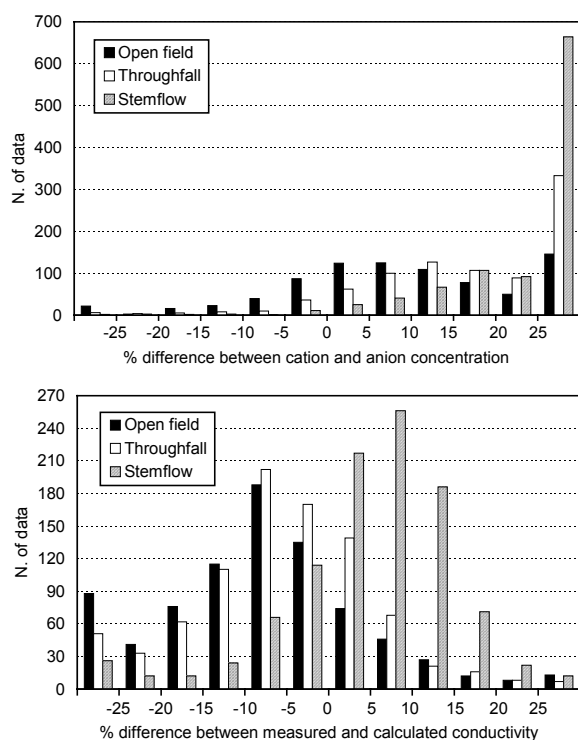

Fig. 6. Check of anion *vs* cation concentrations (upper) and of measured *vs* calculated conductivity (lower) for open field, throughfall and stemflow precipitation.

4.2. Relationships among ions

The correlation among the different ions was established using the volume weighted mean concentrations of all the stations. From the measured values the concentration of organic nitrogen was calculated as difference between TN and $NO_3 + NH_4$, and the value of Δ (μeq l^{-1}), as difference between the sum of cations and anions. Δ should be related to the content of organic acid present in solution, which is not considered in the chemical analyses. On the other hand Δ also includes all the analytical errors made in the determination of the single ions, so that it must be considered only as a rough evaluation of the organic component. The correlation matrix for the three types of deposition, obtained using the Spermann correlation, is presented in tables 6 to 8 for OF, TF and SF concentrations respectively.

The strong influx of the marine component is evident with OF and TF values, and is pointed out by the relationship between chloride and sodium, potassium, magnesium; sulphate also shows a correlation with chloride, which highlights the importance of the natural fraction of sulphate. Hydrogen ion concentration is not linked to any of the ions considered in OF, while in TF it is loosely related to alkalinity, calcium and sodium. Calcium is significantly related to alkalinity, magnesium and sulphate. Ammonium and nitrate are correlated with each other, but do not show any relationship with other ions, even with organic nitrogen, either in OF or TF. On the other hand, in TF organic nitrogen is related to potassium, alkalinity and Δ (organic matter), probably as the effect of leakage from leaves.

In the case of SF, only the relationship between chloride and sodium remains among those linked to the marine contribution, and those linking calcium to magnesium. The relation between Δ and ON, absent in OF and significant at P <0.01 in TF, is significant at P <0.001 in ST, indicating a gradual increase in importance of compounds leached from leaves. This is not completely confirmed by the relationship between Δ and potassium, which is highly significant in TF, but not in SF.

4.3. Flux of ions to the plots

The deposition of ions in the open field is presented in table 9. A comparison of the flux of hydrogen ion and alkalinity shows a net flux of acidity only in two plots: PIE1 and FRI1 (11 and 4 meq m^{-2} y^{-1}). In the remaining areas, net deposition of alkalinity ranges from 1 (FRI2) to 125 (SIC1) meq m^{-2} y^{-1}. However, bulk deposition overestimates alkalinity, as it also includes local dust, which is alkaline in most of the areas. The flux of base cations, which is also influenced by the sampling technique, is altogether high, ranging from 50 meq m^{-2} y^{-1} in FRI2, in northern Italy, to values higher than 100 meq m^{-2} y^{-1} in TOS1, CAM1 and SIC1 (Central and South Italy). Nitrogen, which does not show any great differences of concentration from southern to northern sites, does however show definitely higher fluxes in northern sites (142, 109, 103 mmol m^{-2} y^{-1} respectively in PIE1, LOM1, VEN1), while the lowest values are in central and southern sites (55, 65 meq m^{-2} y^{-1} in SIC1 and LAZ1).

A comparison between the flux in OF and in TF (Tab. 10) shows an increase in most of the ions during the passage of the deposition through the canopy. This is the effect of both dry deposition on the leaves and leakage from the foliar surface, which is responsible for the strong increase of potassium and organic matter, roughly quantified by the difference between cations and anions (Δ). Total nitrogen flux is higher in the TF than in OF, indicating a net release from the canopy; this is true for nitrate and organic nitrogen, while ammonium fluxes show lower values in TF than in OF in several plots.

Tab. 6. Significance of the relationships among ions in bulk open field depositions (Spearman correlation, *: p <0.05; **:p <0.01; ***: p <0.001).

	mm	Cond.	PO4	H+	NH4+	Ca++	Mg++	Na+	K+	Alc.	SO4=	NO3-	Cl-	NT	ON	Δ
mm	-															
Cond.		-														
PO4		*	-													
H+				-												
NH4+					-											
Ca++	*	***				-										
Mg++		***	**			**	-									
Na+		***				***	***	-								
K+		***	*			***	***	***	-							
Alc.		**	**			***	***	**	***	-						
SO4=	*	***				*	**	***	**		-					
NO3-	*			*							*	-				
Cl-		***	*			***	***	***	***	**	***		-			
NT	*				**								***	-		
ON		**								**					-	
Δ		**	**			*	***	***	**	**	**		***			-

Tab. 7. Significance of the relationships among ions in throughfall depositions (Spearman correlation, *: p <0.05; **:p <0.01; ***: p <0.001).

	mm	Cond.	PO4	H+	NH4+	Ca++	Mg++	Na+	K+	Alc.	SO4=	NO3-	Cl-	NT	ON	Δ
mm	-															
Cond.	*	-														
PO4			-													
H+	*	*		-												
NH4+	*				-											
Ca++	***	***		***		-										
Mg++	**	***		*		***	-									
Na+		***				***	***	-								
K+	**	***		*		***	***	***	-							
Alc.	***	***		***	*	***	***	**	***	-						
SO4=	*	***				***	***	***	***	**	-					
NO3-			*		**							-				
Cl-		***		*		***	***	***	***	**	**		-			
NT	*			***		*			*	**	*	**		-		
ON	*	**				***	**		***	**	**				-	
Δ	***	***		**		***	***	*	***	***	***		*		***	-

Tab. 8. Significance of the relationships among ions in stemflow depositions (Spearman correlation, *: p <0.05; **:p <0.01; ***: p <0.001).

	mm	Cond.	PO4	H+	NH4+	Ca++	Mg++	Na+	K+	Alc.	SO4=	NO3-	Cl-	NT	ON	Δ
mm	-															
Cond.		-														
PO4			-													
H+		**		-												
NH4+					-											
Ca++		***		*		-										
Mg++		***				***	-									
Na+							*	-								
K+		**				**	**		-							
Alc.				*						-						
SO4=		***		*		**	**		***		-					
NO3-	*		**		*							-				
Cl-		**				**	**	***					-			
NT					**									-		
ON	*	*							***		**			*	-	
Δ	*	***				**	**		***		***				***	-

Tab. 9. Mean ion deposition in the open field during 1998-1999. ON, TN: organic and total nitrogen. Units: ions: meq m^{-2} y^{-1}, nitrogen compound: mmol m^{-2} y^{-1}, Δ difference between cations and anions, as an estimate of the fractions of organic acids meq m^{-2} y^{-1}. [1]: research performed in 1999; *: corrected for the marine contribution.

	FRI2	LOM1	TRE1	ABR1	CAL1	CAM1	EMI2	PIE1	VEN1	TOS1	EMI1	FRI1[1]	LAZ1	MAR1	SIC1
H$^+$	10	19	2	1	14	6	10	20	9	10	3	10	4	4	7
NH$_4^+$	26	42	35	20	21	24	29	70	47	32	49	26	24	50	13
Ca^{++}	33	56	45	82	81	71	62	41	65	51	34	26	58	67	174
Mg^{++}	10	8	28	12	58	33	20	9	14	28	10	10	24	33	38
Na$^+$	10	13	10	32	166	111	55	15	17	176	20	23	81	123	112
K$^+$	5	4	7	7	43	9	10	6	6	14	4	4	7	9	13
Alk.	11	30	37	59	58	35	29	9	40	37	15	6	24	43	132
SO$_4^=$	38	55	30	31	88	52	51	63	51	65	39	36	47	51	66
NO$_3^-$	26	41	22	26	27	27	37	60	39	31	33	26	28	33	22
Cl$^-$	11	12	11	32	177	120	55	15	18	120	20	25	89	120	122
Δ	7	3	27	6	32	20	13	14	9	56	12	7	12	39	16
ON	11	28	21	13	27	17	6	12	17	0	11	7	13	14	21
TN	63	109	78	59	75	68	72	142	103	0	93	60	65	96	55
Ca*	32	56	45	81	74	66	60	41	64	47	34	17	55	63	170
Mg*	8	5	26	6	23	10	9	6	10	5	6	3	7	9	14
Na*	1	2	1	4	14	8	8	2	1	73	2	1	5	20	8
K*	5	4	7	6	40	7	9	6	6	11	4	3	6	6	11
SO$_4$*	37	54	29	28	70	40	46	61	49	53	37	23	38	39	53

Tab. 10. Mean ion deposition in throughfall during 1998-1999. ON, TN: organic and total nitrogen. Units, ions: meq m^{-2} y^{-1}, nitrogen compound: mmol m^{-2} y^{-1}; Δ: difference between cations and anions, as an estimate of the fractions of organic acids meq m^{-2} y^{-1}; *Qr*: *Quercus robur*; *Qc*: *Quercus cerris*. [1]: research performed in 1999; *: corrected for the marine contribution.

	FRI2	LOM1	TRE1	ABR11	CAL1	CAM1	EMI2	PIE1	VEN1	TOS1	EMII*Qr*	EMII*Qc*	FRII1[1]	LAZ1	MAR1	SIC1
H$^+$	14	6	3	2	6	2	5	15	8	2	3	2	1	4	2	1
NH$_4^+$	25	30	14	39	19	26	31	67	51	46	106	98	20	17	17	28
Ca^{++}	69	64	40	90	116	105	59	47	60	81	69	69	54	67	105	166
Mg^{++}	33	18	22	35	86	71	31	13	24	104	32	31	31	41	49	83
Na$^+$	17	14	8	55	208	199	63	16	18	213	30	25	19	99	156	168
K$^+$	47	56	24	67	106	65	47	33	45	76	53	47	40	41	63	109
Alk.	7	23	24	87	68	73	42	15	36	95	63	65	44	24	64	130
SO$_4^=$	75	50	23	37	122	76	54	63	64	101	74	60	36	53	61	83
NO$_3^-$	43	46	14	25	23	47	46	67	48	46	71	54	20	37	41	16
Cl$^-$	25	16	11	67	239	222	73	17	21	181	37	34	26	118	175	214
Δ	55	52	40	70	89	51	23	30	35	102	47	59	39	37	53	111
ON	38	39	22	55	43	29	18	21	29	0	29	22	18	22	29	39
TN	106	115	51	120	85	102	94	154	128	0	206	174	57	77	87	84
Ca*	68	63	39	87	107	97	57	47	60	75	67	68	53	63	98	158
Mg*	28	15	20	22	39	28	17	10	19	69	24	24	26	18	15	41
Na*	0	0	0	0	5	9	2	1	0	58	1	0	0	0	6	0
K*	47	55	24	66	102	61	46	33	44	73	52	46	40	39	60	105
SO$_4$*	72	49	22	31	97	53	46	61	62	82	70	56	33	41	43	61

Stemflow fluxes, measured in 8 plots (Tab. 11), show values which are far lower than TF and OF fluxes. The relative importance of OF compared with TF ranges from less than 1% to 10%; the lowest values are measured in conifer stands (FRI2 and TRE1), while the values are higher and in the same range for *Fagus sylvatica* and *Quercus* sp. stands.

Eventually, an attempt was made to evaluate the total flux of ions related to acidification, considering the sum of the deposition of ammonium, nitrate and sulphate. The production of acidity per mole of ammonium was assumed as 1.5, as an average between 1, in the case of uptake from vegetation, and 2, in the case of oxidation to nitrate (Reuss & Johnson 1987; van Breemen *et al*. 1984). The fraction deriving from sea spray was subtracted from sulphate; nevertheless it must be borne in mind that a further fraction of sulphate may be due to volcanic emissions (SIC1, CAL1) and to minerals transported from North Africa (Guerzoni & Chester 1996; Loye-Pilot & Martin 1996; Carratalà *et al*. 1996), events which are quite frequent in South and Central Italy, and which not infrequently affect even the northernmost stations.

The deposition of compounds related to acidification (DEP acid) was calculated in the open field and in the plot, as the sum of throughfall (TF) and stemflow (SF):

Tab. 11. Mean ion deposition in stemflow during 1998-1999. ON, TN: organic and total nitrogen. Units, ions: meq m^{-2} y^{-1} nitrogen compound: mmol m^{-2} y^{-1}, Δ difference between cations and anions, as an estimate of the fractions of organic acids meq m^{-2} y^{-1}; *Qr: Quercus robur; Qc: Quercus cerris*. [1]: research performed in 1999; *: corrected for the marine contribution.

	FRI2	TRE12	ABR1	CAL1	CAM11	EMI2	PIE11	VEN1	TOS1	EMI1*Qr*	EMI1*Qc*	LAZ1
H$^+$	0.2	0.01	0.0	0.0	0.2	0.3	0.3	0.1	0.1	0.1	0.1	0.7
NH$_4^+$	0.1	0.00	0.2	0.1	0.5	2.5	4.8	0.3	0.4	5.6	5.1	1.4
Ca^{++}	0.7	0.05	1.6	1.4	2.7	3.9	2.0	1.0	5.6	1.1	3.0	10.0
Mg^{++}	0.3	0.02	0.7	1.2	2.6	1.9	0.7	0.3	5.3	0.6	1.0	7.4
Na$^+$	0.1	0.00	1.7	3.8	10.4	6.6	0.8	0.3	9.9	1.0	1.1	22.9
K$^+$	0.8	0.06	1.6	2.3	1.5	4.5	5.3	1.4	7.3	3.2	5.9	11.3
Alk.	0.0	0.00	1.0	0.3	0.6	1.6	1.5	0.6	2.6	1.0	2.7	1.3
SO$_4^=$	0.9	0.04	0.9	2.4	2.7	5.1	4.7	0.9	6.6	2.7	3.4	9.7
NO$_3^-$	0.1	0.00	0.5	0.0	1.3	3.7	4.9	0.3	1.5	2.8	3.0	6.7
Cl$^-$	0.3	0.01	2.0	4.2	10.3	7.1	0.9	0.4	10.2	1.2	1.2	25.6
Δ	1.0	0.09	1.5	1.8	3.0	2.1	2.0	1.1	7.6	4.0	5.9	10.4
ON	0.5	0.03	0.9	0.7	0.7	0.8	1.4	0.9	0.0	1.4	1.9	5.1
TN	0.6	0.03	1.5	0.9	2.5	7.0	11.0	1.5	0.0	9.7	9.9	13.2
Ca*	0.7	0.05	1.6	1.3	2.4	3.6	2.0	1.0	5.2	1.1	3.0	9.0
Mg*	0.3	0.02	0.3	0.4	0.5	0.5	0.5	0.2	3.3	0.3	0.8	2.3
Na*	0.0	0.00	0.1	0.2	1.5	0.5	0.0	0.0	1.2	0.1	0.0	1.0
K*	0.8	0.06	1.6	2.2	1.3	4.4	5.3	1.4	7.1	3.2	5.9	10.9
SO$_4$*	0.9	0.04	0.7	2.0	1.6	4.4	4.6	0.9	5.6	2.5	3.3	7.0

Tab. 12. Volume (mm) and deposition of acid ions (SO$_4^=$, NO$_3^-$, NH$_4^+$), alkalinity, total nitrogen and base cations (BC: mmol m^{-2} y^{-1}) in the CONECOFOR research areas. *Qr: Quercus robur, Qc: Quercus cerris.*

|		08 FRI2	10 LOM1	17 TRE1	01 ABR1[1]	03 CAL1	04 CAM1	06 EMI2	12 PIE1	20 VEN1	16 TOS1	05 EMI1*Qr*	07 FRI1	05 EMI1*Qc*	09 LAZ1	11 MAR1	15 SIC1
volume	1998	1335	1593	1048	591	1257	850	845	1252	1203	717	567	-	567	906	1038	582
	1999	1489	2157	1135	567	1848	1428	1433	1995	1530	1006	929	961	929	1077	1166	544
acid ions	1998	98	136	81	79	93	71	90	170	143	132	119	-	119	90	170	70
	1999	104	180	125	89	164	136	164	281	174	131	166	142	166	114	123	118
alkalinity	1998	15	30	27	79	35	45	18	6	49	23	14	-	14	23	64	54
	1999	7	30	47	40	81	26	40	12	31	51	17	9	17	25	21	210
total N	1998	65	67	55	55	55	48	56	112	94	672	84	-	84	58	106	56
	1999	62	151	101	63	96	88	87	172	111	582	101	86	101	73	87	54
BC	1998	59	57	95	151	275	172	106	64	104	310	62	-	62	116	196	198
	1999	57	105	86	115	421	277	188	80	99	227	75	88	75	225	268	477
BC*	1998	50	44	88	112	119	91	70	53	92	158	44	-	44	68	118	102
	1999	42	90	68	82	183	91	101	57	71	112	48	46	48	77	79	302
Throughfall + Stemflow																	
volume	1998	1050	1303	864	840	1162	937	614	1280	1529	553	551	-	528	906	859	621
	1999	1165	1738	857	714	1240	1148	1214	2043	1596	846	836	744	1251	1035	1006	601
acid ions	1998	110	126	53	137	142	130	105	176	199	201	231	-	224	113	104	105
	1999	198	152	63	114	159	154	194	312	177	209	309	165	405	127	115	134
alkalinity	1998	9	35	26	77	73	78	28	9	19	82	48	-	56	14	79	92
	1999	5	10	21	100	64	69	60	23	54	113	88	88	71	36	48	168
total N	1998	84	117	47	153	86	92	78	123	136	1022	172	-	168	83	85	71
	1999	128	114	55	91	86	116	124	207	123	852	196	115	264	97	89	96
BC	1998	124	138	97	273	529	466	146	102	137	439	167	-	148	213	328	376
	1999	213	167	91	232	519	450	291	136	162	568	198	289	231	387	419	675
BC*	1998	111	121	90	189	273	209	102	90	121	258	137	-	118	116	198	193
	1999	180	147	77	168	240	190	158	108	131	324	159	238	182	170	160	415
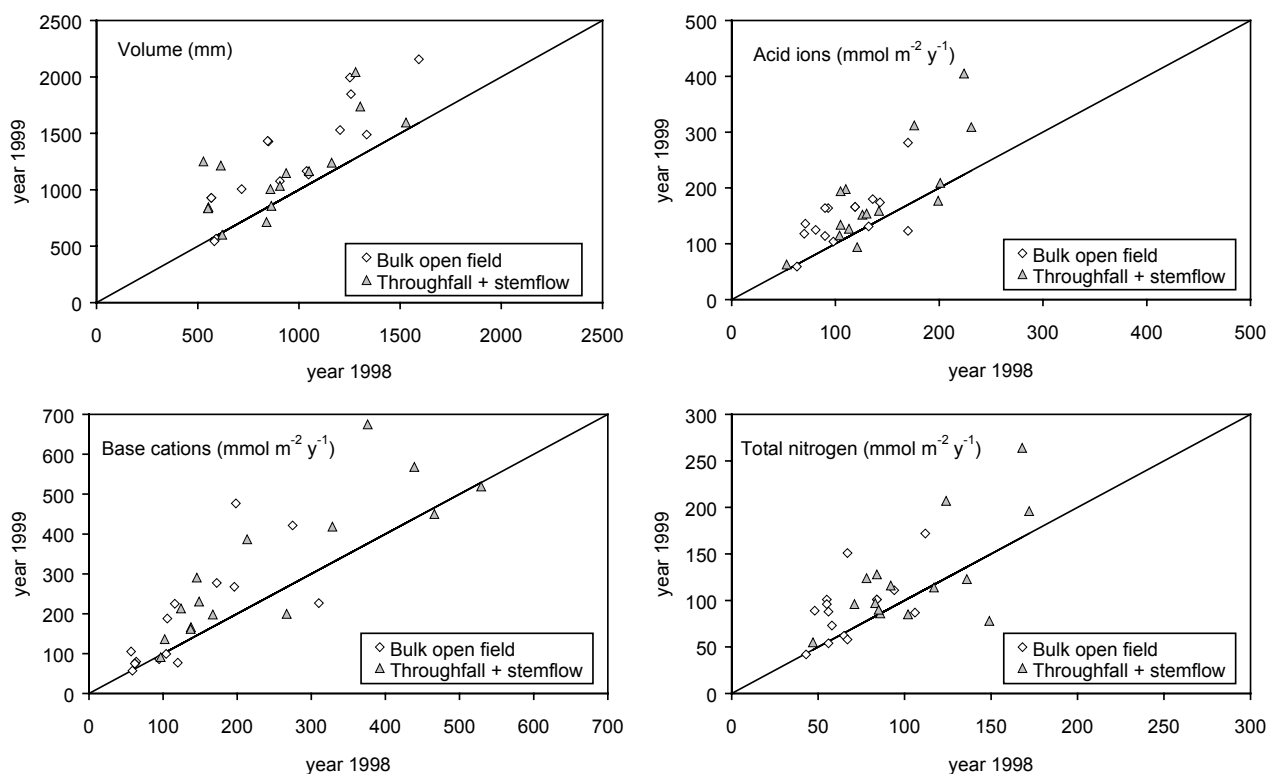
Fig. 7. Comparison between 1998 and 1999 values of amount of precipitation (mm) and deposition of acid ions, base cations and total nitrogen.

$$DEP_{OF} (acid) = 2\ DEP_{OF} (SO_4^*) + DEP_{OF} (NO_3) + {} + 1.5\ DEP_{OF} (NH_4)$$

$$DEP_{IF} (acid) = 2\ DEP_{TF} (SO_4^*) + 2\ DEP_{SF} (SO_4^*) + {} + DEP_{TF} (NO_3) + DEP_{SF} (NO_3) + {} + 1.5\ DEP_{TF} (NH_4) + 1.5\ DEP_{SF} (NH_4)$$

where units are mmol m^{-2} y^{-1}. It must be emphasised that these values do not express actual or potential acidity, as most of the anions are buffered by the high concentrations of calcium and other base cations.

Results (Tab. 12) shows the highest values in open field (130-280 mmol m^{-2} y^{-1}) in the northern sites of PIE1, VEN1, LOM1; the station of MAR1, located in Central Italy, also shows high values, mainly due to high ammonium deposition. The lowest values (70-130 mmol m^{-2} y^{-1}) were measured in the plots TRE1, ABR1, CAM1, SIC1. The ranking is very similar in the case of total deposition (Tab. 8), with a ratio total/OF ranging between 0.8 to 1.9.

The difference in ion fluxes between the two study years (Fig. 7) in most of the stations shows slightly higher values in 1999 than in 1998, both for OF and TF+SF deposition, in accordance with the high volumes of precipitation.

4.4. Nitrogen saturation

Besides the alkaline/acidic input in deposition, the deposition of nitrogen, sometimes referred to as the "eutrophication effect" (e.g. Posch *et al*. 1999) must be taken into account. Also in this case we considered the OF and the deposition in the plot, as follows:

$$DEP_{OF} (N) = DEP_{OF} (NO_3) + DEP_{OF} (NH_4)$$

$$DEP_{IF} (N) = DEP_{TF} (NO_3) + DEP_{SF} (NO_3) + {} + DEP_{TF} (NH_4) + DEP_{SF} (NH_4)$$

where units are mmol m^{-2} y^{-1}. Results show a wide range of variation both for OF and in the plot values (Tab. 12). The ranking of the values is close to those of acidic compounds, with the highest values of OF nitrogen deposition in the areas PIE1, MAR1 and VEN1 (94-172 mmol m^{-2} y^{-1}), while the lowest are in TRE1, ABR1, LAZ1 (55-101 mmol m^{-2} y^{-1}). The ratio between the OF and total deposition of nitrogen ranges between 0.8 and 3.4.

Nitrogen loads may be compared with nitrate and total nitrogen concentrations in stream waters. To synthesise the concentrations and the seasonal variations of nitrate we used the Stoddard & Traan approach (Tab. 13), as applied to water courses with frequent samplings (Traan & Stoddard 1995; Stoddard 1994). This ap-

Tab. 13. Nitrogen saturation stage criteria for stream with frequent samples. The criteria are based on monthly average NO_3^- concentration (Traaen & Stoddard 1995).

Stage	Criteria	Meaning
0	More than 3 months in the growing season with NO_3^- <3 and no value >20 $\mu eq\ l^{-1}$.	Nitrogen cycle dominated by forest and microbial uptake.
1	1-2 months in the growing season with NO_3^- <3 $\mu eq\ l^{-1}$ or more than 3 months in the growing season with NO_3^- <3 $\mu eq\ l^{-1}$ and one value >20 $\mu eq\ l^{-1}$	Watershed proceeds toward saturation: nitrate concentration frequently exceeds typical values
2	No month with NO_3^- <3 and more than 3 months in the growing season with NO_3^- <50 $\mu eq\ l^{-1}$	Nitrogen cycle dominated by loss through leaching and denitrification
3	more than 3 months with NO_3^- >50 $\mu eq\ l_1$	Amplification of stage 2: deposition, mineralization and nitrification contribute nitrate to leaching waters

proach gives a quantification of the level of nitrogen saturation of the watershed; the higher the stage of saturation, the lower the possibility of soil and vegetation to metabolise and immobilise the amount of nitrogen deposited from atmosphere. Results (Fig. 5) give a saturation stage of 1 for sites FRI2 and PIE1, stage 2 for EMI2, stage 3 for PIE1. These values mean that all the areas are subjected to nitrogen overload, very accentuated in the case of EMI2 and PIE1, and that vegetation and soil microflora are no longer able to regulate the nitrogen flux. These conclusions are further supported by the high organic nitrogen content, which is present in the highest amounts in the two streams with relatively low nitrate.

5. CONCLUSIONS

1998 and 1999 were the first full years when data on the chemistry of atmospheric deposition were collected in Italy. For this reason, sampling, analysis and data validation were performed with particular care and in strict accordance with international standards (UN-ECE 1994). The sampling stations considered, all located in permanent plots for the study of vegetation growth and evolution, are representative of different geographical conditions, from the Mediterranean conditions of the southern sites to the Alpine environment of some of the northern stations. The chemistry of bulk deposition is strongly influenced by natural sources, such as the marine component (Na, Cl, Mg, part of the sulphate) and soil dust (Ca, alkalinity, Mg, K), of local or remote origin (North Africa). Among the changes due to anthropogenic emissions in the atmosphere, acidification is present in some of the northern stations (PIE1, FRI2), while most of the other sites show a net flux of alkalinity, even in open field deposition. The acidity is however buffered by the dust and dry deposition present on the canopy, so that the throughfall deposition is always alkaline. However, it must be emphasised that bulk deposition is not entirely reliable in estimating the acidity level of deposition, as it is strongly influenced by dust particles of local origin. The parallel measurement of wet deposition in some areas has already been planned, with the aim of improving our understanding of the relative importance of local and transported substances in atmospheric deposition.

An estimation of the amount of ion deposition related to anthropogenic emissions (sulphate, nitrate and ammonium, Fig. 8) produces a wide range of variations, with the highest values in the northern (PIE1, VEN1) and central (EMI1, TOS1) sites and the lowest in the southern and alpine stations. The contribution of volcanic emissions to the high sulphate deposition of CAL1 and SIC1 requires further investigation.

The situation of nitrogen deposition is far more critical: values are very high both in open field and TF samples. Again, there is a trend towards lower values in the southern and central stations than in the north of the country. Both ammonium and nitrate are important in OF deposition; the importance of organic nitrogen increases markedly in the TF and SF samples, if compared with OF. The different level of nitrogen deposition is clearly reflected in the nitrate and total nitrogen concentrations of the stream water sampled in four plots, quantified through the Stoddard and Traaen approach (Fig. 5). The plots show a release of nitrate from the watershed in all seasons, indicating an overload of nitrogen compared to its possible uptake by vegetation, but saturation is very high, also in absolute terms (stage 3 of the Stoddard & Traaen criteria) in the northern plot PIE1, high in the central EMI2 plot (stage 2), and moderate in the central and alpine plots of LAZ1 and FRI2. Furthermore, a comparison between actual and critical loads of acidity and nitrogen, detailed in a previous paper (Mosello & Marchetto 1999), reveals nitrogen load exceedances in most of the areas.

Nitrogen enrichment is a common feature of large parts of Europe with intensive human activities; its impact on surface and drinking water poses a serious challenge. The gradient shown in these four Italian sites offers an opportunity to study details of the processes of deposition and transformation of the different N species immediately after deposition, pointing out the interactions existing between nitrogen deposition, vegetation uptake and release in surface water.

Other aspects of the relationships between atmospheric deposition chemistry and vegetation status are being considered in the interdisciplinary project CONECOFOR, and form the basis for Italian forestry research, in close connection with the international
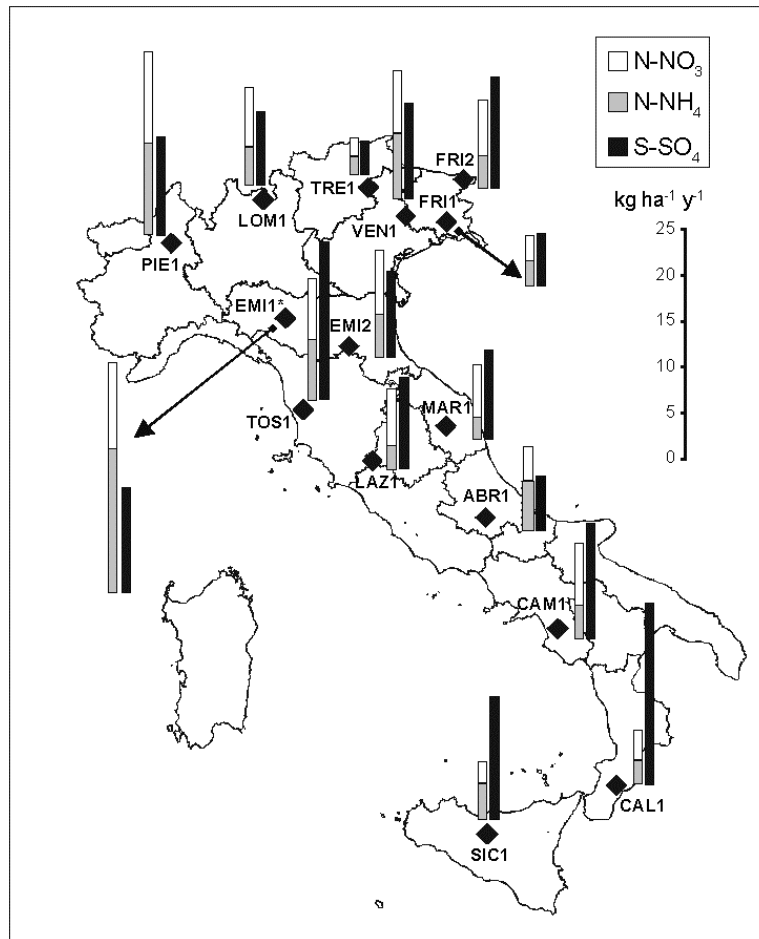
Fig. 8. Open field bulk depositions of sulphate, nitrate and ammonium in the Italian sampling sites.

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