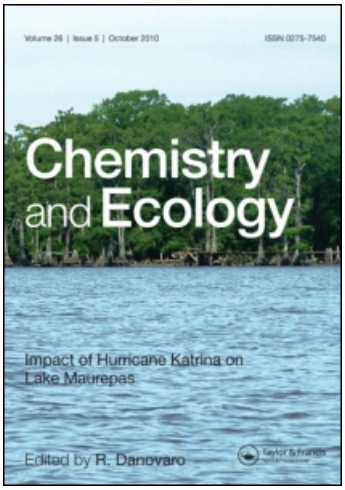

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ACID DEPOSITION IN THE TUSCAN APPENNINES DURING THE DRY PERIOD 1988–89.

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The typical parameters of acid precipitation are evaluated in the forest of Vallombrosa (Tuscan Appennines) during the dry period 1988–89. Individual rain events (dry and wet deposition) were sampled in a clearing of the forest and below the canopy of an evergreen tree as well as a deciduous broadleaf tree.

In atmospheric precipitation the pH values usually vary around 4.4, with neutralization in the hot season due to calcareous material from distant sources. Relatively large concentrations of Pb and Cd are found in rain, but only in a small amount in canopy leachate. Aluminium, manganese and iron are more significantly washed off than Pb and Cd.

KEY WORDS Acid deposition, rainwater composition, wet-dry deposition, atmospheric pollution, canopy leaching.

INTRODUCTION

The role that acidic precipitation plays in forest decline has already been pointed out by several authors (Evans, 1984; Fluckiger *et al.*, 1986; Gellini *et al.*, 1987; Matzer and Ulrich, 1985; McFee *et al.*, 1977; Schutt and Cowling, 1985). The acidity of polluted precipitation — especially fog, which produces H^+ concentrations 10 to 100 times higher than rain (Brewer *et al.*, 1983; Fuzzi *et al.*, 1985, 1988; Munger *et al.*, 1983) — is the cause of physiological damage in forest ecosystems. A significant acid deposition has been measured in some damaged Tuscan forest zones, which are far from main roads and heavy traffic (Barbolani *et al.*, 1986; Pantani *et al.*, 1984). The forest disease observed in Vallombrosa (Tuscan Appennines) over several years (Pantani *et al.*, 1985) has prompted measurement of levels of acidity and pollutants in rainwater samples (bulk and occasionally dry deposition) taken in this area. The chemical composition of atmospheric precipitation has already been analyzed (Barbolani *et al.*, 1988) with pH values in rainwater often in the range 4–4.5, with partial neutralization by atmospheric dust during the hot season.

The area of Vallombrosa, an environmentally valuable zone, makes necessary a

continuous watch for early detection of possible causes of forest disease. In this framework the aim of the present paper is to extend the investigation to wet only deposition as well as to the presence of micropollutants such as heavy metals in rainwater. Further, the winter 1988–89 examined here was marked by a climatically unusual drought, so the analytical data obtained are of wider interest.

As acid deposition can increase leaching from trees of easily mobilised elements (Evans *et al.*, 1981; Hoffman *et al.*, 1980; Paoletti *et al.* 1989a, b; Hindawi *et al.*, 1980; Johnson *et al.*, 1983; Leonardi *et al.*, 1989; Wood *et al.*, 1975; Zoettl and Huettl, 1986), throughfall samples under the crown of *Tilia cordata* L. (with falling leaves in autumn) and *Abies alba* L. have also been collected and analyzed.

EXPERIMENTAL METHODS

Sampling

Samples of rain water were taken during 15 months between March 1988 and June 1989, considering the period March 16 to October 15 as "hot season" and October 16 to March 15 as "cold season". A severe drought occurred between the two summer solstices. Several collectors were positioned as in previous investigations (Barbolani *et al.*, 1988): the first (station 1) in a clearing of the forest, the second (station 2) beneath the crown of *Tilia cordata* L., and the third (station 3) beneath the crown of *Abies alba* L., to evaluate canopy leaching.

Samples of wet only deposition were taken during single events. On the whole, samples were obtained for the majority (a total of 50) of the precipitation events taking place during the period. For each event, a single polypropylene container, pre-cleaned and conditioned in the laboratory and conserved in a clean polyethylene bag, was used.

In order to determine the real representativity of the samples, the samplers, after the removal of the rain water, were washed with 0.01 M nitric acid to remove particles adherent to the walls. In samples below pH 5.6, some components (mainly alkaline earth metals) can be lost by their adherence to the walls and are usually reduced by 2–5%, as a mean of more than 20 cases. In neutralized samples, a higher amount can be lost due to precipitation of basic compounds.

Samples were filtered on 0.45 μm membrane and stored in polyethylene bottles at +4°C. A portion was acidified to pH = 3 with HNO_3 suprapur Merck for determination of heavy metals. Conductivity, $[H^+]$ and $[NH_4^+]$ were determined immediately after filtration. Filtered samples were stable for more than a week. During this period the reproducibility of measurements is better than 3%.

At the same stations, during periods without rain, the dry deposition was collected. The sample collectors were mounted on an orbital agitator with 100 ml of superpure H_2O (obtained from an Elga UHQ system) for two hours, and the resulting liquid was then analysed as the wet deposition.

Analysis

The analysis of Cl^-, SO_4^{2-}, NO_3^-, PO_4^{3-} was carried out by ion chromatography using a Dionex mod. 4000i chromatograph in conjunction with an H.P. mod. 3396

A integrator. A conductometric detector following chemical suppresion of eluent conductivity was the response system, using a Dionex AS4A column and $NaHCO_3$ 1.7×10^{-3} M + Na_2CO_3 1.8×10^{-3} M as eluent.

The metals were determined with a Perkin–Elmer 2380 Atomic Absorption Spectrophotometer with an acetylene–air flame (Na, K, Ca, Mg) or HGA 400 Graphite Furnace and AS 40 Autosampler (Fe, Mn, Cu, Al, Cd, Pb) using the normal procedure (Perkin–Elmer, 1980).

Potentiometric titrations of free acidity were performed using an Orion Microprocessor Ionalyser mod. 901 connected with a Beckman mod. 39524 glass electrode.

An ion selective electrode Orion mod. 9512 was used for NH_4^+ determination.

Conductivity measurements were carried out with a conductometer Metrohm mod. E 527 with a cell Metrohm mod. 6.0904.040.

RESULTS AND DISCUSSION

The results of pH measured in the 50 samples from the clearing, representing wet only deposition, confirmed the presence of free acidity (pH≤5.6) in 37 cases, about three quarters of the total (Figure 1): the fact that the sampling period was predominantly rain-free, unusual especially during winter, did not result in significant differences from previously reported trends (Barbolani *et al.*, 1988; Pantani *et al.*, 1985). The tendency for neutralized rains to accumulate during the warmer periods, and particularly during the beginning of spring, is still evident, even though the overall scatter of data is significant.

The majority of rain events was of limited duration; 17 were below 5 mm and 19 between 5 and 10 mm. The possibility of neutralization was increased for these brief rainfalls in comparison to the usual pattern of precipitation. A possible

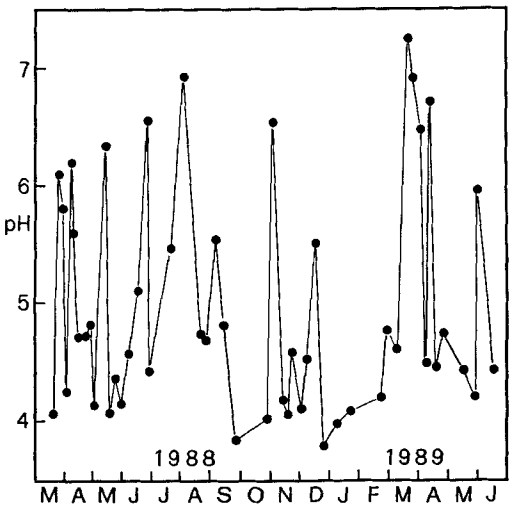

Figure 1 pH values in rain water samples (station 1).

Table 1 Data on acidity in samples at the 3 stations

	Station 1	*Station* 2	*Station* 3
All samples (498.0 mm):			
pH, average	4.44	4.90	4.72
weighted average	4.51		
median	4.66	5.49	5.15
electr. cond., K_{25}	58.60	95.30	119.90
Acidic samples (417.2 mm):			
pH, average	4.31	4.81	4.65
weighted average	4.44		
median	4.43	5.30	5.03
electr. cond., K_{25}	48.20	80.40	106.90
Hot season (303.0 mm):			
pH, average	4.49	5.28	5.19
Cold season (195.0 mm):			
pH, average	4.39	4.71	4.48

factor could be the atmospheric washout of relevant quantities of alkaline neutralizing dust in a small rain volume.

The mean pH values, calculated from the average of the H^+ concentrations, and still more the median values (Table 1), seem to indicate overall an acidity which is slightly lower than that reported in previous investigations. Even so, the peak values should also be considered, in that it is in these events where we must presumably search for the cause of forest damage. The mean of samples which present free acidity can also be taken into consideration.

Fourteen of the fifty total samples were found to have a pH less than 4.2, with a mean of 4.04; these figures pertain to only 93 mm of rainfall. If forest damage

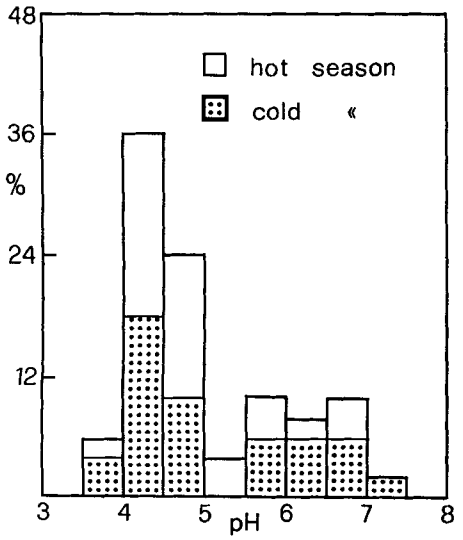

Figure 2 Distribution of rain water samples (station 1) in classes of half pH units.

Table 2 Concentrations in mg/l of the major inorganic components in rainwater at the 3 stations

	Station 1		*Station* 2		*Station* 3	
	average	*median*	*average*	*median*	*average*	*median*
Na^+	2.51	0.83	6.33	2.43	7.80	4.23
K^+	0.60	0.35	3.21	2.21	5.46	3.51
Ca^{2+}	2.54	0.91	4.99	3.76	6.18	3.59
Mg^{2+}	0.58	0.17	1.58	0.88	1.91	1.12
Cl^-	6.26	1.34	12.24	3.81	12.25	5.97
SO_4^{2-}	6.12	4.77	9.87	8.43	14.73	10.54
NO_3^-	3.30	2.69	6.39	2.57	11.95	3.94
PO_4^{3-}	2.21	2.60	0.84	0.68	0.34	0.32

can be imputed to an elevated level of localized acidity, brief rainfalls with lower pH become much more relevant.

The grouping of samples in classes which differ by a half-unit of pH (Figure 2) shows the already noted distribution, apparently bimodal, with a minimal probability of finding samples around pH 5.5 where buffer capacity exhibits its minimum and where there is a greater susceptibility to neutralization or acidification.

The mean values of the concentrations found for the major inorganic components are shown in Table 2. The most interesting conclusions are illustrated in the following three figures. Figure 3 shows the variation of the ratio between calcium and magnesium in conjunction with the variation of the pH of the sample. It is evident that the median value, reported in Figure 3, is higher in the case of neutralized water, confirming that the neutralizing agent is composed essentially of calcareous dust. Also significant is the alteration of the same ratio in favour of magnesium, which occurred when rain events were associated with winds of marine origin, rich in sea salt aerosol. Although less evident, the increment of the ratio between sulphate and nitrate with pH value (Figure 4) indicates a higher presence of sulphate in the neutralizing material. The ratio for samples of pH <5.6, just under 2, fits the general pattern of relative proportions of the two acids, sulphuric and nitric, still in favour of sulphuric acid, but with a

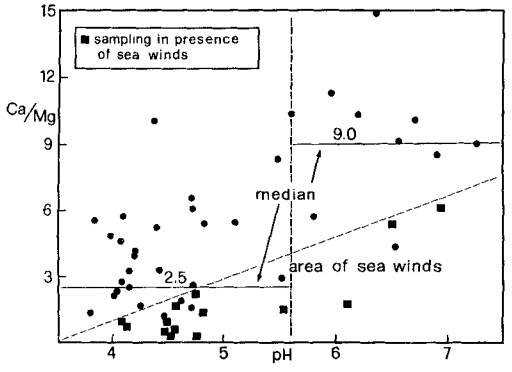

Figure 3 Values of the ratio (in equivalents) Ca/Mg vs. pH of rain water samples (station 1). The dashed line separates acidic from neutralized samples.

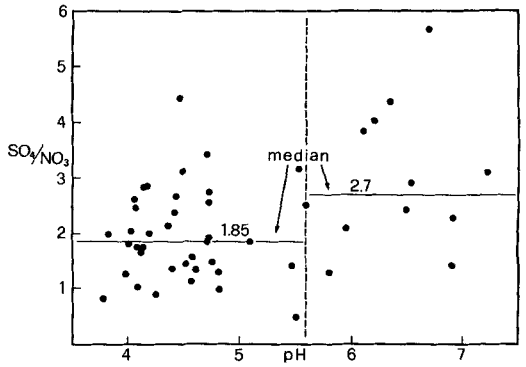

Figure 4 Values of the ratio (in equivalents) SO_4^{2-}/NO_3^- vs. pH of rain water samples (station 1). The dashed line separates acidic from neutralized samples.

notable increase of nitric acid in rain samples during the past few years, so that the ratio draws closer to 1.

And finally, the ternary diagram in Figure 5, the percentages of the three main anions shows that nearly all the data points are crowded in the upper right half of the diagram, confirming once again the preponderance, with respect to nitrates, sulphates or chlorides, according to the absence or presence of sea winds. Neutralized samples are found mainly in the small area to the extreme right.

Tables 1 and 2 report the concentrations of inorganic components found in the water gathered beneath the crown of deciduous and coniferous trees, an index of foliar leaching by atmospheric precipitation. The concentrations are higher relative to the composition of wet only deposition sampled in the clearing, as is to be expected with the mobilization of deposited materials from the canopy, including materials left by dry deposition; the abnormal increment of potassium is notable, in particular.

Mean data for dry deposition are shown in Table 3. Dry deposition, in effect, as pointed out in previous studies (Barbolani *et al.*, 1988), shows no free acidity,

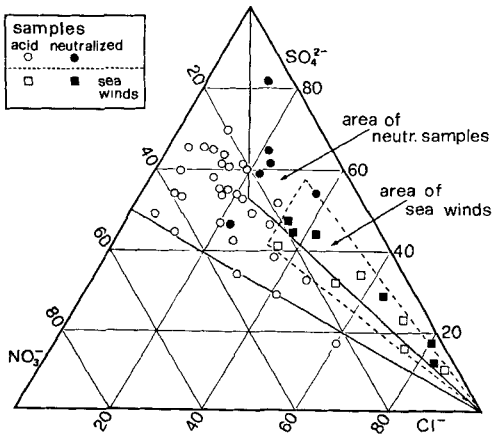

Figure 5 Percentage distribution of the three main anions (in equivalents) in ternary diagram.

Table 3 Amount of dry deposition, reported in mg/m^2-year, at the 3 stations

	Station 1	*Station 2*	*Station 3*
Na^+	131.1	50.9	51.9
K^+	207.7	141.2	70.7
Ca^{2+}	309.2	234.9	195.0
Mg^{2+}	41.2	29.9	22.1
Cl^-	174.8	78.5	81.2
SO_4^{2-}	326.7	118.4	94.3
NO_3^-	150.0	99.8	71.5

with the exception of a few samples collected during the cold season. Contrary to wet deposition, samples gathered beneath the crown showed lower concentrations for all the components, a phenomenon which can be attributed to the screening effect of the crown.

As far as heavy metals are concerned, the analytical results show a great variability and a little correlation with pH. In Table 4 aluminium and iron are seen to be present at higher concentrations than the other heavy metals (Pb, Cu, Mn and Cd). In the most acid samples, mainly in those of lower average quantity of precipitation, there is a tendency towards higher concentrations. This is

Table 4 Median values of the concentrations ($\mu g/l$) of heavy metals in rainwater for groups of samples at different pH

	pH of the samples			
	any	<= 5.6	<= 4.7	<= 4.2
N. of samples	46	34	22	13
mm, total	461.2	390.2	178.8	82.4
mm, median	7.1	7.9	7.3	5.6
Al^{3+}	23.9	17.7	22.2	24.8
Pb^{2+}	5.3	8.7	13.3	18.2
Cu^{2+}	2.9	2.3	2.6	3.2
Mn^{2+}	4.9	4.3	4.1	6.4
Fe^{3+}	19.2	25.8	24.2	23.4
Cd^{2+}	1.6	1.9	2.2	1.9

Table 5 Concentrations of heavy metals ($\mu g/l$) in rainwater (Station 1) and in canopy leaching (Stations 2 and 3)

	Station 1		*Station 2*		*Station 3*	
	average	*median*	*average*	*median*	*average*	*median*
Al^{3+}	32.9	23.9	50.9	34.3	104.9	49.0
Pb^{2+}	10.3	5.3	3.9	3.8	3.9	2.5
Cu^{2+}	4.1	2.9	4.1	2.7	4.7	2.9
Mn^{2+}	8.1	4.9	23.9	12.5	27.9	19.3
Fe^{3+}	40.2	19.2	38.7	20.5	56.1	34.0
Cd^{2+}	3.7	1.6	3.8	0.9	0.9	0.7

particularly evident for lead which tends to hydrolyze in the samples with higher pH values and therefore cannot be found in solution.

In analysing the scavenging action of the crown (Table 5) one can draw a distinction between aluminium, manganese and iron which are more significantly mobilized in canopy leachate than Pb, Cd and Cu.

CONCLUSIONS

The summary of the data contained in this study wholly confirms the concern expressed of the acid deposition phenomenon in the forest area in the Appennines in central Italy. The unusually dry period examined here does not seem to have affected significantly the accumulation of the pollutants present in the atmosphere and consequently in rain water. In reality, those rain events which are least important from a quantity point of view should be considered more seriously for possible effects on the forest ecosystem on account of their elevated concentration of free acidity. One cannot ignore, in addition, the diffuse presence of concentrations of heavy metals, both those of anthropogenic origin such as lead and cadmium, and those like aluminium and manganese whose rain-induced leaching and mobilization has been proposed as a cause of plant damage (Krug and Frink, 1983; Mayer and Ulrich, 1977; Scherbatskoy and Klein, 1983; Ulrich *et al.*, 1980).

Given the complexity of natural events such as precipitation, the data of this study, while offering sound information on the conditions in the Vallombrosa area, require further investigation pertaining to other macro- and micro-pollutants (including organic substances) before one can specifically attribute forest decay there to atmospheric contamination.

Acknowledgment

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