Chemical characterization of cloud episodes at a ridge site in Tuscan Appennines, Italy

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Abstract

Cloudwater samples were collected from November 1992 to March 1995 in Vallombrosa, a mountain site of the Tuscan Apennines (central Italy). Chemical analyses show that all examined inorganic ions contributed significantly to the total ionic content (TIC). The ratio SO_4^{2-}/NO_4^- ranged from 0.92 to 3.46 and was >1 for 86% of samples. There is a wide range in the chemical composition of the cloudwater. The total ionic content ranged from 640 to 7476 μeq l^{-1} and pH from 3.17 to 6.22. The liquid water content (LWC) ranged from 0.06 to 0.94 g m^{-3} and electrical conductivity from 47 to 485 $\mu\Omega^{-1}$. The total ionic content decreases while the liquid water content increases. Also analyzed were soluble trace metals (Fe, Pb, Cu, Mn, Cd, Al), synthetic anionic surfactants and the methanesulphonic acid. Chemical analyses evidenced in some cases a high concentration of organic matter. The meteorological analysis for a few samples of individual passages was carried out for the possibility of establishing a correspondence between meteorological

events and chemical composition. The sources (marine, crustal and anthropogenic) of chemical components were deduced. © 2002 Elsevier Science B.V. All rights reserved.

1. Introduction

The chemical composition of cloudwater depends on many factors, such as chemical characteristics of the parent air mass (pollution situation at backward trajectory, etc.), cloud dynamics (entrainment rate, updraft and turbulence within the cloud, etc.) and microphysics [liquid water content (LWC), droplet size distribution, phase partitioning, etc.]. Cloud droplets formed via condensation of water vapour (nucleation) on aerosol particles are called cloud condensation nuclei (CCN). The droplet growth depends on the size and chemical composition of the particles and on the supersaturation of the water vapour.

Moreover, droplets can absorb gaseous chemical species and scavenge particles through Brownian diffusion, inertial, diffusio-thermophoretic and electrostatic capture. Once chemical species are incorporated into the aqueous phase, chemical reactions may occur.

Previous researchers (Flossmann et al., 1985; Noone et al., 1988; Baechmann et al., 1996; Collett et al., 1999; Ogawa et al., 1999; Menon et al., 2000) showed that cloud droplets of different sizes may have different solute concentrations. Results are partially contradictory, as measurements present both increasing and decreasing solute concentrations with increasing droplet diameter. The results from measurements in the Po Valley show a strong decrease in droplet ionic concentrations with increasing diameter (Ogren et al., 1992), whereas the results from the measurements at the mountain station Kleiner Feldberg show both increasing, as well as decreasing, solute concentrations with increasing droplet diameter (Wobrock et al., 1994). Collett et al. (1993), at the mountain station of Mt. Rigi in Switzerland, showed that droplets smaller than 10 μm were enriched in NO_3^-, SO_4^{2-} and NH_4^+ compared to larger droplets. Schell et al. (1997), at the summit station of Great Dun Fell in the north of England, found higher solute concentrations in larger droplets for droplets that were relatively young and formed by orographic lifting and suggested that droplet growth time is an important factor for the size dependence of solute concentration. For more aged clouds, solute concentration decreased with an increase in diameter. Schell et al. (1997) also suggested that the increased solute concentrations found in smaller droplets could result from entrainment when new particles enter the cloud and form new droplets.

Most ions are significantly more concentrated in nonprecipitating clouds with respect to precipitating ones (Falconer and Falconer, 1980; Mohnen and Kadlecek, 1989; Khwaja et al., 1995; Möller et al., 1996). Therefore, at high sites, the exposure of plants to acute pollutant levels is more likely to occur through cloud droplet interception than through precipitation.

As well as dry and wet deposition, the importance of the cloudwater deposition process in forest decline was reported earlier (Lovett, 1984; Pahl and Winkler, 1995; Saxena et al.,

1989; Vong et al., 1991). Several investigations have shown that the amount of cloudwater deposited onto forests increases with height due to increasing LWC, wind speed and the shift of the droplet spectrum to larger droplets (Lovett and Kinsman, 1990; Lin and Saxena, 1991). An attempt is presented to give an explanation for the presence of heavy metals even in marine clouds by considering the production mechanism of marine aerosol. This may derive from the bursting of bubbles produced by the entrainment of air at the wave crests. Film drops, jet drops and shearing drops originating from strong winds can evaporate to give aerosol particles. Adsorption of natural and man-made surfactants [surfactant organic matter (SOM)], on the surface of bubbles, also heavily increases the concentration of pollutants, which are able to interact with them, for example, heavy metal ions (MacIntyre, 1972; Blanchard, 1975; MacCarthy, 1989; Frimmel and Abbt-Braun, 1993; Cini and Loglio, 1997; Cini et al., 1998; Oppo et al., 1999).

The outcome of the overall study is also expected to permit a better understanding of the causes of forest decline.

2. Experimental

In Vallombrosa, a mountain site of the Tuscan Apennines (950 m asl, 43°N, 11°E), a cloudwater collector device (MTX CNB1000) was located in the period of time from November 1992 to March 1995 (Fig. 1). The sampler is based on the aerodynamic capture
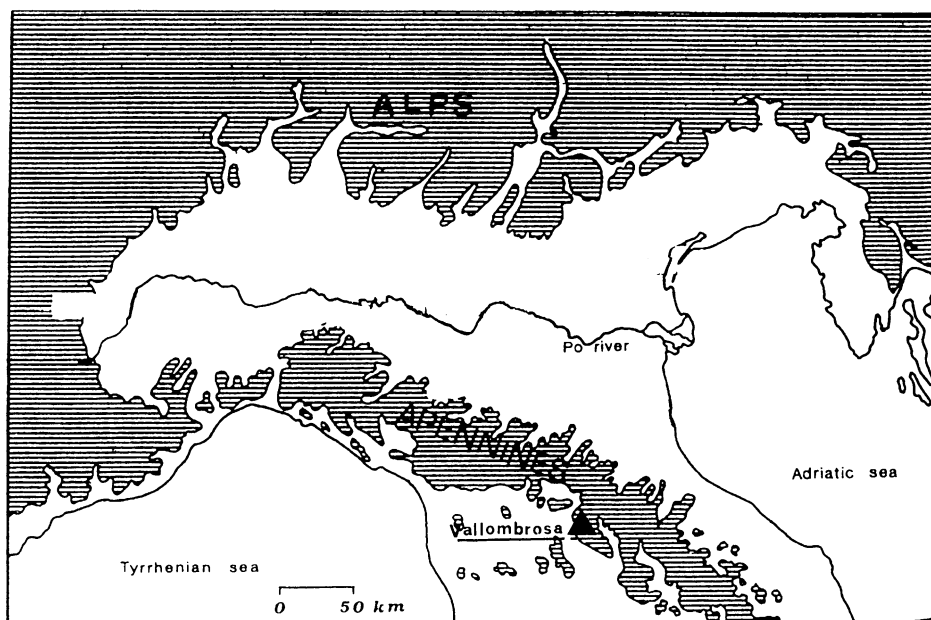

Fig. 1. Map of northern and central Italy showing cloud sampling site. The shaded area indicates elevations greater than 500 m.

of cloud droplets and consists of a short wind tunnel in which an air stream containing the droplets is created by a fan located in the rear part of the tunnel. The droplet impact on a series of Teflon strings 0.4 mm thick, which are arranged in form of screens strung on three frames inclined at an angle of $30°$ with respect to the direction of the flow. Once the droplets are collected, they coalesce with each other and are pulled by gravity and aerodynamic drag into the collection funnel and a polyethylene sample bottle. The mean speed of the air is 6 m s^{-1}. The theoretical 50% size cut of each individual string corresponds to a drop radius of 2.5 μm, while the overall efficiency is ca. 43% (Fuzzi et al., 1996). The collector is sealed at both ends by two covers, which are automatically opened only when the collector receives the consensus for sampling from the micro-processor controller and the fan is also switched on. Fog and rain optical sensors are present on top of the collector to activate the device with the arrival of the cloud (due to increased extinction of the medium) and to interrupt collection in case of rain, respectively. The sampling device stopped the operation of the collection when the temperature fell below freezing. The Teflon wire frames of the sampling apparatus and the walls of the tunnel were carefully washed with distilled deionized water before each set of sampling operations.

Cloudwater collected in a polyethylene bottle was filtered through a 0.4-μm Nuclepore filter and stored at 4 °C until analysis.

The analytical determinations were carried out by potentiometric and conductimetric methods (pH and conductivity), as well as ion chromatography. The pH was measured by a model Orion PH-meter, equipped with a Ross electrode, more reliable for low-ionic content solutions. A model 120 Analytical Control conductivity meter was used to measure sample conductivity (corrected to 20 °C). The ionic content was determined using an integrated system of three ion chromatographs with conductivity detectors. The columns used for the separations were Dionex AS12A (Cl$^-$, SO$_4^{2-}$, NO$_3^-$), Dionex AS11 (MSA) and CS12A (NH$_4^+$, Ca^{2+}, Mg^{2+}, Na$^+$, K$^+$). The sample containers were opened under a class 100 laminar hood and filtered on a 0.45-μm Teflon membrane filter, just before analysis. To avoid uptake of NH$_3$ from the atmosphere, the plastic cylinders containing the liquid sample were maintained in a bag filled with NH$_3$-free air. Blank control procedures, sample treatment and IC methods are described elsewhere (Udisti et al., 1991, 1994). The linearity range, the detection limit (as two times the standard deviation of 10 blank measurements) and reproducibility (as percentage standard deviation of 10 measurements of a standard solution containing 10 μg l^{-1} of ionic species) were determined for ion chromatographic measurements. The detection of dissolved Fe, Pb, Cu, Mn, Cd and Al (defined as the fraction that passes through a 0.45-μm filter) was performed by means of absorption atomic spectroscopy (Perkin Elmer mod.2380 with graphite furnace). The injected sample volume was typically 20 μl and three replicates were made for every sample. In this way, the reproducibility was around 2–3% and the detection limits were in the range 0.5–2 μg l^{-1} for the measured metals. A deuterium lamp, for background correction, was used where possible. The concentrations of surfactants were detected as methylene-blue active substances (MBAS) (Longwell and Maniece, 1955). The measurements of natural surfactants [surfactant fluorescent organic matter (SFOM)] were done with a Perkin Elmer LS50B fluorescence spectrometer (Cini et al., 1998). The ionic balance for every sample was calculated to check analysis reliability. Data quality

Table 1a

Inorganic chemical composition of samples collected during cloud events (unit: ion concentration, μeq l^{-1}; conductivity, $\mu\Omega$ cm^{-1}; LWC, g m^{-3})

Sample	Starting date	pH	H$^+$	NH$_4^+$	Ca^{2+}	Mg^{2+}	Na$^+$	K$^+$	Cl$^-$	SO$_4^{2-}$	NO$_3^-$	LWC	Conductivity	TIC	PDI (%)
1	10/11/92	4.53	29.5	188.8	162.6	82.3	397.8	56.0	402.4	342.9	195.2	0.241	97.4	1904	0.5
2	26/11/92	5.63	2.3	100.1	147.6	88.1	561.8	31.5	527.7	201.9	200.0	n.d.	100.8	1904	2
3	11/12/92	6.19	0.6	35.0	117.7	35.4	238.2	31.0	155.7	99.9	80.0	0.943	43.7	891	5
4	29/12/92	3.21	616.6	643.0	72.8	38.7	174.4	29.4	162.5	690.1	708.1	0.092	341.0	3201	0.6
5	21/01/93	3.58	263.0	175.2	27.9	15.6	75.7	4.9	94.3	334.2	141.5	0.210	114.8	1161	1.3
6	8/04/93	3.17	676.1	1286.7	165.1	82.3	306.1	38.4	281.9	1285.8	917.8	0.101	390.0	5037	1.3
7	11/04/93	3.92	120.2	107.3	30.9	9.1	33.9	8.7	31.0	210.3	70.6	0.336	70.0	640	2.3
8	11/06/93	3.58	263.0	910.5	313.2	85.5	209.6	52.2	158.5	1269.3	371.0	0.109	228.2	3660	2
9	12/11/93	6.18	0.7	102.3	136.6	39.5	171.7	29.4	82.2	139.8	145.2	0.158	47.1	913	8
10	10/12/93	3.31	489.8	324.7	134.6	481.5	2251.0	98.7	2566.5	643.2	456.5	0.055	485.0	7476	2
11	17/12/93	3.54	288.4	250.3	74.6	144.8	634.8	22.8	676.1	353.8	272.1	0.120	214.0	2737	5
12	12/01/94	3.94	114.8	126.6	40.9	51.0	244.8	23.5	272.3	184.0	116.1	0.151	92.4	1184	3
13	12/02/94	3.24	575.4	460.6	113.2	65.8	266.5	18.9	305.3	562.7	611.3	0.085	n.d.	3012	1
14	18/03/94	3.22	602.6	605.1	115.2	31.3	113.5	14.1	117.4	781.0	517.8	0.225	315.0	2940	3.7
15	10/05/94	4.31	49.0	406.9	148.6	31.3	84.8	20.7	79.1	391.0	250.0	0.161	106.6	1494	3.6
16	25/05/94	3.75	177.8	256.0	78.3	51.0	177.8	14.1	182.5	393.1	157.9	0.184	127.1	1508	2.6
17	13/09/94	6.22	0.6	247.4	110.2	18.9	55.7	49.6	48.7	187.9	123.6	0.221	55.3	940	3.6
18	9/11/94	3.26	549.5	324.3	63.8	55.1	279.1	26.1	315.2	520.5	369.4	0.092	271.0	2557	5.7
19	18/2/95	4.16	69.2	444.9	50.9	42.8	231.7	22.8	189.8	470.3	216.1	0.245	106.3	1812	3.3
20	17/3/95	4.45	35.5	278.9	46.4	27.2	230.9	15.9	196.3	293.4	98.4	0.136	92.7	1287	8.6

n.d.: no data.

control was performed evaluating the percentage difference of the ionic balance (PDI) calculated as:

$$\text{PDI} = (\text{Conc.}_{\text{anions}} - \text{Conc.}_{\text{cations}})/\text{Conc.}_{\text{anions}} + \text{Conc.}_{\text{cations}}) \times 100$$

The acceptability criterion was set: PDI $\leq \pm 10\%$.

The PDI values are reported in Table 1a.

Collected samples may come from one single cloud passage of short duration or from several passages of variable duration. In the latter case, the confluence of cloudwater in the same bottle hinders the possibility of assigning the chemical composition to a specific event and the average concentrations are difficult to interpret in terms of air mass origin. Conversely, a sample resulting from a single cloud passage has a peculiar meaning for the purpose of relating composition to meteorological situation and cloud type.

Thus, the samples can be separated into two groups: those representative of an individual cloud passage (or almost), and those representative of many events.

The detailed meteorological analyses have been carried out for only a few samples of individual passages for the possibility of establishing a correspondence between meteorological events and chemical composition.

Sources for meteorological analyses are:

- conventional meteorological data (radiosoundings launched at some European stations) and surface and absolute topographies of isobaric maps
- infrared, visible and water vapour Meteosat images

The purpose is to reconstruct the origin of the air mass in which the sampled clouds originated. Isothermopotential curves are obtained from radiosoundings. Potential temperature (θ) is a conservative property in adiabatic processes and helps in identifying the air masses: in isentropic processes, the curves of constant θ are also air mass trajectories. The satellite images have been processed by bidimensional histograms for characterizing, for example, cloud top temperatures. There are several factors that limit the accuracy of trajectory calculations. First, the isentropic formulations require adiabatic flow, which is a good first approximation, above the turbulent surface mixed layer and away from any deep convective cells. Then, we will consider only air mass trajectories that do not pass through convectively active regions.

3. Results and discussion

3.1. Cloudwater chemical composition of samples

Inorganic chemical composition, pH, the total ionic content (TIC, sum of the main inorganic ions), LWC and electrical conductivity of samples collected during all non-precipitating cloud events are reported in Table 1a, while the synthetic anionic surfactants (as MBAS) and the methanesulphonic acid (MSA) data are reported in Table 1b. The samples sometimes represent a single event and sometimes several events with different air masses.

Table 1b
Chemical concentration of MBAS and MSA (unit: $\mu g\ l^{-1}$) in samples collected during cloud events

Sample no.	MBAS	MSA
1	960	64.9
2	460	23
3	270	12.8
4	260	70.8
5	210	30.8
7	42	34.2
9	n.d.	26.8
10	110	73.8
11	n.d.	54.2
12	n.d.	23.6
13	n.d.	66.3
14	170	n.d.
16	100	n.d.
17	75	n.d.
18	96	n.d.
20	70	n.d.

n.d.: no data.

With a few exceptions (sample nos. 2, 3, 9 and 17), the pH values are less than the CO_2 equilibrium value of 5.6. The pH range is from 3.17 to 6.2. Numerous investigators report data on cloud acidity and chemistry of cloudwater collected at mountain sites (Okita, 1968; Möller et al., 1994; Fuzzi, 1994; Acker et al., 1995; Weathers et al., 1995). Kroll and Winkler (1990) reported a maximum SO_4^{2-} concentration of just over 1000 $\mu eq\ l^{-1}$ for a set of 193 cloudwater samples collected at Grosser Arber (1090 m asl) in the Bavarian forest (Germany). Collett et al. (1993) (Seeboden, 1030 m asl, in central Switzerland) measured the following average, minimum and maximum concentration ($\mu eq\ l^{-1}$) for H^+: 5, 0.2, 166; NH_4^+: 920, 150, 6600; SO_4^{2-}: 380, 37, 2500; NO_3^-: 440, 19, 3700. Na^+ and Cl^- ion concentrations were much lower than the Vallombrosa values.

For comparison, we report in addition, the measurements obtained by Ogren and Rodhe (1986) during the summers of 1983 and 1984 at a clean air site in the mountains of central Scandinavia. H^+, NH_4^+, Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, NO_3^- and SO_4^{2-} concentrations are, respectively, in $\mu eq\ l^{-1}$, 13, 0.5, <0.4, <0.8, <0.2, 0.3, 0.8, 2 and 6, when air is from the Arctic, while the values are 370, n.d., 33, 6, 12, 22, 19, 68 and 700 $\mu eq\ l^{-1}$ when air is from the industrial regions of Europe.

A comparison of ion concentrations in cloudwater sampled at Vallombrosa with those observed at other locations reveals that the considered region is exposed to significant pollutant levels and that it is influenced by sea components.

We can observe that in our samples, all examined ions contributed significantly to the total ion concentration. Previous researches (Weathers et al., 1988; Mohnen and Kadlecek, 1989; Collett et al., 1990a; Saxena and Lin, 1990; Khwaja et al., 1995) conducted in mountain areas show on the contrary that SO_4^{2-}, NO_3^-, NH_4^+ and H^+ are the principal ions reflecting, in this case, the dominant influence of anthropogenic sources

on the cloudwater chemistry. Plessow et al. (2001) performed cloud investigations at Mt. Broken (Central Germany). On average, contributions of SO_4^{2-}, NO_3^- and NH_4^+ to TIC run up to 86% for all samples. Kim and Aneja (1992) (Mt. Mitchell, 2038 m asl, in the Mt. Mitchell State Park, USA), during one orographic cloud event (nonprecipitating), found that H^+, NH_4^+, SO_4^{2-} and NO_3^- were the major constituents, accounting for about 98% of the total analyzed ions. In our samples, the total concentration for the same ions ranges from 24% to 85% with respect to TIC. The average, minimum and maximum concentrations for H^+, NH_4^+, SO_4^{2-} and NO_3^- measured at Vallombrosa were, respectively (μeq l^{-1}), H^+: 246, 0.6, 676; NH_4^+: 364, 35, 1287; SO_4^{2-}: 468, 100,1286; NO_3^-: 301, 71, 918.

The ratio of SO_4^{2-} and NO_3^- ranges from 0.92 to 3.46 and is >1 for 86% of samples. This dominance of sulphate over nitrate indicates that SO_4^{2-} primarily contributed to the acidity of cloudwater. Similar results have been found in other areas (Weathers et al., 1988; Saxena and Lin, 1990; Minami and Ishizaka, 1996; Kmiec et al., 1997). However, Collett et al. (1993) and Fuzzi (1994) reported nitrates dominating over sulphates in cloudwater in Sierra Nevada and at Kleiner Feldberg, respectively.

The NH_4^+ concentration is well correlated with the sum of $NO_3^- + SO_4^{2-}$ ($r = 0.95$) (Fig. 2). This indicates that ammonium sulphate and nitrate aerosols contribute to a large fraction of these anions. In Fig. 3, we observe that the sum of SO_4^{2-} and NO_3^- ion concentration is higher than that of H^+ and NH_4^+, with a correlation coefficient $r = 0.98$. Consequently, some other cations from alkaline substances must be responsible for neutralizing the excessive anions, for example, Ca^{2+}.
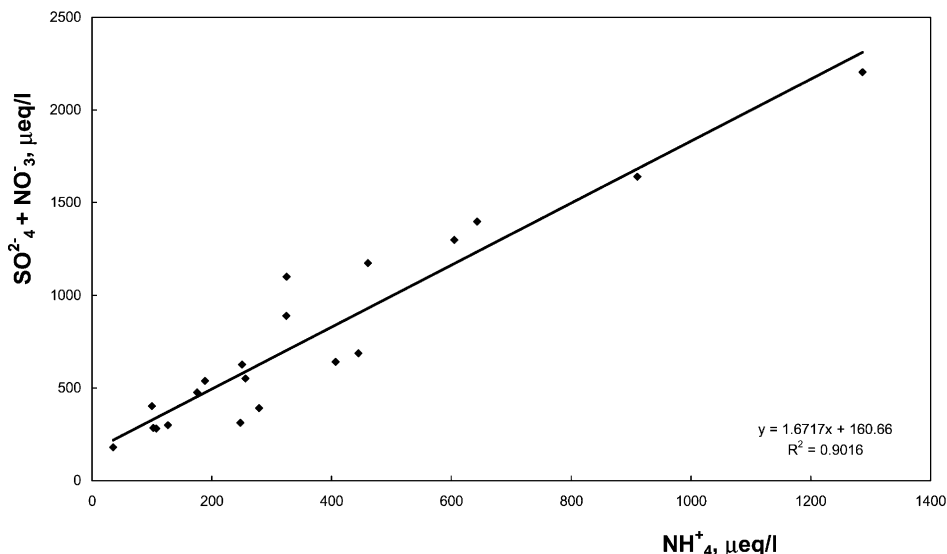

Fig. 2. Concentrations of NH_4^+ ions versus ($SO_4^{2-} + NO_3^-$) in cloudwater collected from passage events. The data are from Table 1 in the respective columns for the 20 samples.

Fig. 3. Concentrations of $(NH_4^+ + H^+)$ ions versus $(SO_4^{2-} + NO_3^-)$ in cloudwater collected from passage events. The data are from Table 1 in the respective columns for the 20 samples.
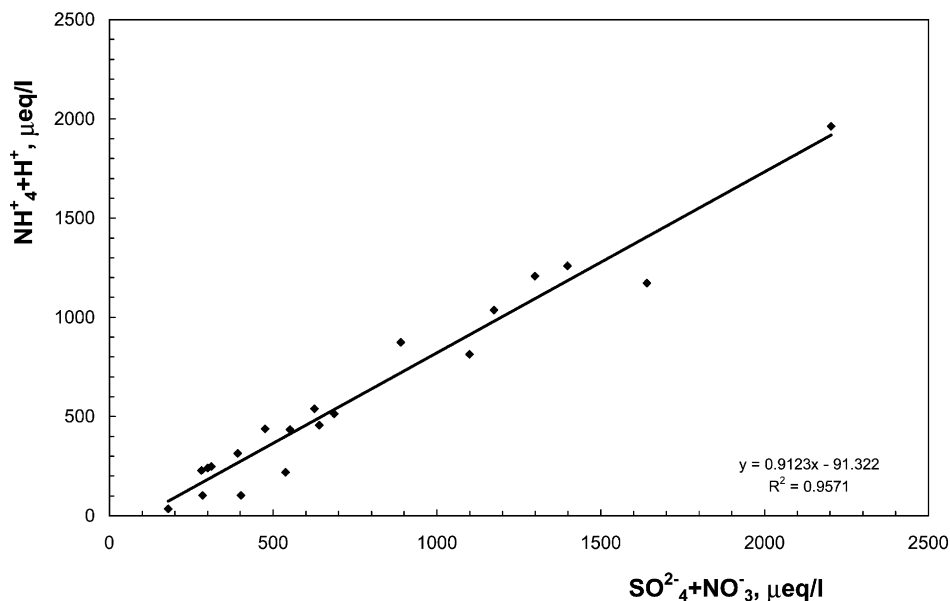
As illustrated in Fig. 4a and b, SO_4^{2-} and NO_3^- are negatively correlated with the pH of the cloudwater. To explain this trend, we observe that sulphate ion in cloudwater can be attributed to an input of gaseous sulphuric acid, scavenging of aerosol particles containing sulphate or to oxidation of inorganic or organic S compounds. In fact, most particulate sulphate is emitted indirectly into the atmosphere, resulting from the oxidation of SO_2, either as a homogeneous gas-phase reaction (photochemical oxidation, oxidation with free radicals or molecules) or as a heterogeneous reaction on the surface of solid aerosols and in atmospheric water droplets (uncatalyzed oxidation, oxidation catalyzed by metallic contaminations such as Fe^{3+}, Mn^{2+} and Cl^- ions or soot). Sulphate-coated aerosols, related to cloud processing of dust particles, are frequently observed in the Mediterranean (Wurzler et al., 2000).

In addition, a source of non-sea salt SO_4^{2-} (nss-SO_4^{2-}) is from the oxidation of dimethylsulfide (DMS) released by the biogenic activity on the marine surfaces. This is confirmed by the abundant traces of MSA ($13-74$ μg l^{-1}) present in all the cloud samples in which the analytical procedure of MSA was performed, since MSA is formed (together with SO_2) after the gas-phase oxidation of DMS. This oxidation process increases the H^+ concentration; that is, lowers the pH of droplets.

The Cl^- catalytic activity for SO_2 oxidation has been demonstrated by several researchers (Clarke and Radojevic, 1983; Santachiara et al., 1991; Zhang and Millero, 1991). Measurements in coastal areas seem to confirm the importance of this process (Cass and Shair, 1984). As Cl^- concentrations measured in our samples range from about 50 to 2600 μeq l^{-1}, this ion could catalyze the SO_2 oxidation, in addition to Fe^{3+} and Mn^{2+}.

(a)

$y = 20.576x^{-0.274}$
$R^2 = 0.6547$

SO^{2-}_4, μeq/l

(b)

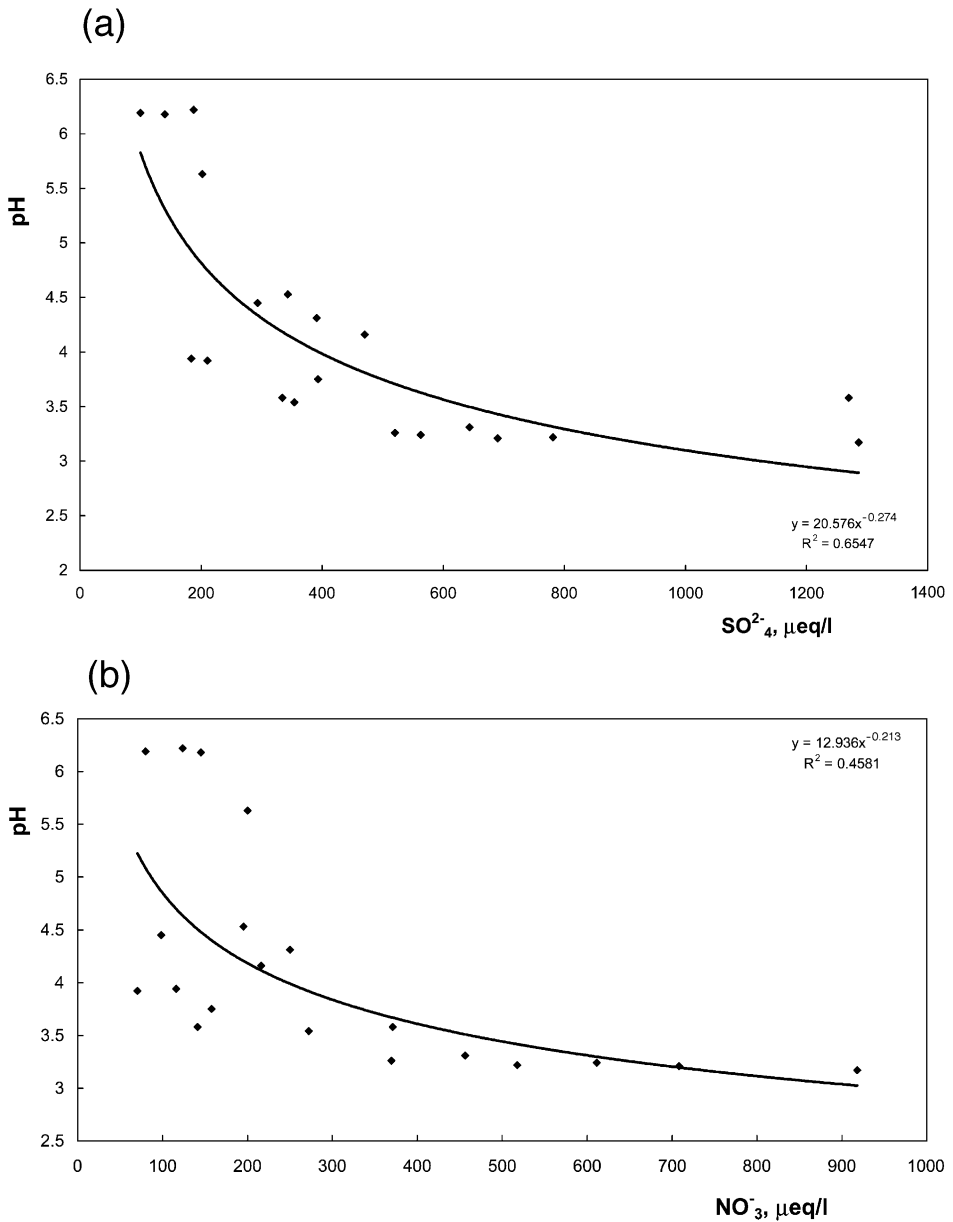$y = 12.936x^{-0.213}$
$R^2 = 0.4581$

NO^-_3, μeq/l

Fig. 4. (a) Relationship between pH and SO_4^{2-} for selected cloud events. The data are from Table 1 in the respective columns for the 20 samples. (b) Relationship between pH and NO_3^- for selected cloud events. The data are from Table 1 in the respective columns for the 20 samples.

Nitrate can be used as a tracer of anthropogenic pollution and can be derived from a direct input of gaseous nitric acid, scavenging of nitrate-containing aerosol, or oxidation of NO_2 dissolved in liquid water.

Cloudwater NH_4^+ concentrations in the droplet may originate from the scavenging of aerosol particles resulting from the reaction between NH_3 and HNO_3 or H_2SO_4, or its presence may be due to the direct uptake of NH_3 by the cloud drops. NH_3 is attributed mostly to bacterial production from agricultural activities and partly to man-made pollutants.

3.1.1. Relationship between chemical composition of cloudwater and LWC

The LWC is an important parameter that influences the chemical composition. The Junge (1963) formulation for nucleation scavenging implies that the concentration of cloudwater solute varies with the inverse of LWC. Since LWC typically increases with height above cloud base due to increased supersaturation, the concentration of any solute with a substantial aerosol phase precursor should decrease with height above cloud base. Deviation from the Junge theory should depend on dissolution of gases, chemical reaction inside cloud droplets and air entrainment.

The results of many LWC measurements for different low-level cloud types and LWC profiles through clouds have been published.

Minami and Ishizaka (1996) analyzed fog water near the summit of Mt. Norikura in Japan (2770 m asl). In the examined events, the concentration of Na^+ and SO_4^{2-} generally showed linearity with 1/LWC, which reflects the dominance of evaporation and condensation processes.

Kmiec et al. (1997) during measurements campaign at Mt. Szrenica (1362 m asl, Poland) obtained, for short-term cloud events, the following physical relationship between TIC and LWC in cloud:

$$TIC = aLWC^b \tag{1}$$

where $a = 88\,700$, $b = -0.78$, TIC in µeq l^{-1} and LWC in mg m^{-3}.

Möller et al. (1996) collected samples from nonprecipitating clouds at Mt. Brocken (Germany) and obtained Eq. (1), where $a = 48\,599$, $b = -0.72$ ($r = 0.52$).

In our samples, LWC ranges from 0.06 to 0.94 g m^{-3} and the conductivity from 47 to 485 µΩ^{-1} cm^{-1}.

In general, an increase in LWC matches a lower conductivity, TIC and a higher pH. The relationship between TIC and LWC based on all considered events (Fig. 5) is given by the previous equation ($r = 0.73$), with $a = 92\,011$ and $b = -0.76$.

The same trend is observed for SO_4^{2-}, NO_3^- and NH_4^+ ions. The parameters a and b of Eq. (1) for SO_4^{2-}, NO_3^- and NH_4^+ ions, are 5084, -0.58; 3473, -0.56; and 2573, 0.49, respectively.

As regards to H^+, the influence of LWC is more limited, as its concentration is determined by the balance between acidic and basic input in the aqueous phase. Thus, it does not automatically follow that more polluted samples will be more acidic.

As an exponent of 1 for LWC should indicate that the dominant processes are dilution and concentration of droplets due to water evaporation and condensation, the relation
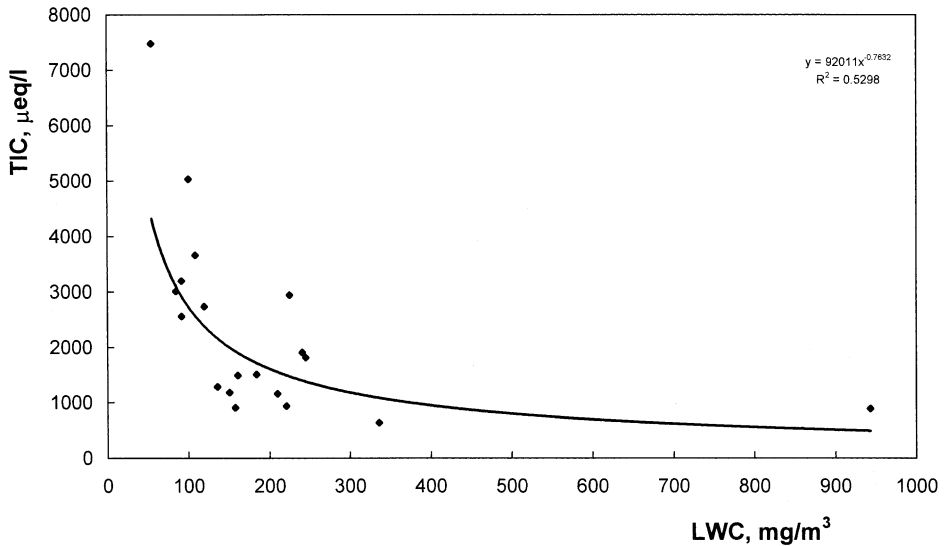
Fig. 5. Relationship between total ionic content (TIC) and liquid water content (LWC) for all samples.

obtained between TIC and LWC indicates the effect of additional factors, that is, scavenging processes, liquid-phase chemical reaction and air entrainment into the cloud.

To obtain the total solute mass in cloud droplets within an air parcel, it is necessary to multiply the TIC by the LWC. Total loading, that is, the sum of solute mass in cloudwater and interstitial mass, is not known in our case as interstitial air concentrations were not measured. We did not find a correlation between the loading in the liquid phase and LWC (Fig. 6).

A logarithm relation was found by Möller et al. (1996). A higher loading of pollutants in clouds, when LWC is higher, was measured also by Fuzzi et al. (1994), on the mountain Kleiner Feldberg, Germany (825 m asl).

Collett et al. (1990b) sampled clouds intercepting the mountain slope (Ash Mountain, Central California). In the examined events, during period of higher LWC, the cloudwater loading of nitrate, sulphate and ammonium increases; when LWC drops, the cloudwater loading generally falls.

The researchers attributed this trend to nucleation scavenging of smaller aerosol size due to increased supersaturation, which determines an increase of LWC and cloudwater loading.

As a matter of fact, in clouds where LWC increases with the altitude above cloud base, the increased loading of material dissolved in cloudwater for given air mass characteristics may depend not only on gas scavenging and oxidation processes in the liquid phase, but also on an increased nucleation scavenging of smaller aerosol particles due to higher supersaturation. As regards to our measurements campaign, this process should occur, in the case of marine clouds, for the finest marine aerosol particles composed of soluble surfactants, produced by the collapse of air bubbles rising to the sea surface (Cini and Loglio, 1997).
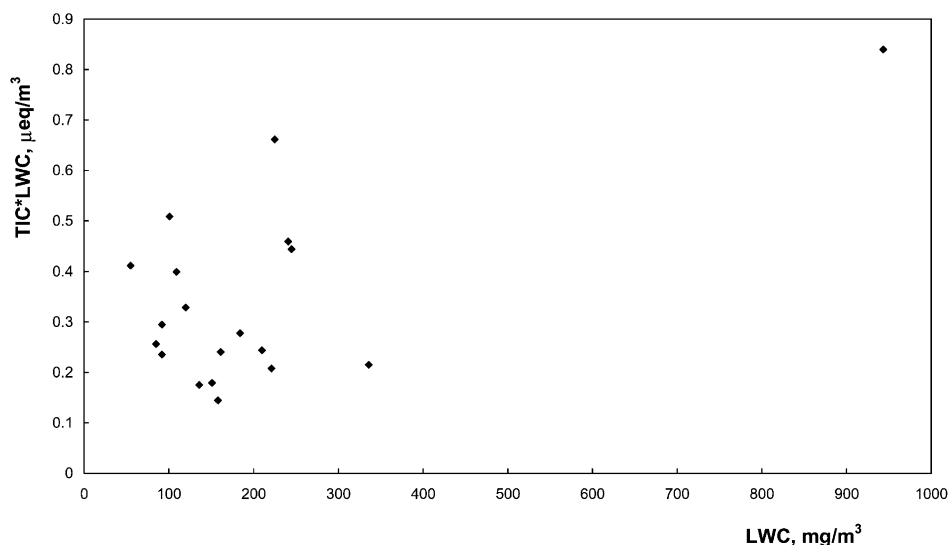
Fig. 6. Total solute mass in cloud droplets per unit volume of air versus liquid water content for selected events.

3.1.2. Sources of elements mainly present in soluble form

For Cl^-, SO_4^{2-}, Ca^{2+}, Na^+ and Mg^{2+}, there is a general agreement that they are essentially water soluble (>90% dissolved). Tanaka et al. (1981) indicate a very small insoluble fraction (<1%) for K^+, Na^+, Mg^{2+}, Ca^{2+} and Cl^- in a marine site, while following Colin et al. (1990), K^+ can reach 12%. To examine the possible sources (marine, crustal or anthropogenic) of chemical components, the enrichment factor (EF) parameter is usually defined:

$$EF(X) = (X/Me)_{aer}/(X/Me)$$

where $(X/Me)_{aer}$ is the weight ratio of any element X with respect to the reference element Me in the aerosol, and (X/Me) is the corresponding ratio in seawater or in the crust. For marine sources, Na is usually the reference element, while for crustal sources, Me can be Al, Fe or Si. EF to Na for Cl^-, SO_4^{2-}, K^+, Ca^{2+} and Mg^{2+}, regarding the examined samples, are reported in Table 2.

Seawater as mass ratios are, respectively: $Cl^-/Na^+ = 1.8$; $SO_4^{2-}/Na^+ = 0.25$; $K^+/Na^+ = 0.036$; $Ca^{2+}/Na^+ = 0.038$; $Mg^{2+}/Na^+ = 0.108$. Considering the mass ratio Cl^-/Na^+ in cloud droplets, we observe in our samples that it is in the range $0.74-1.92$, always less than the seawater ratio (except for sample 5). In addition to marine origin, Cl^- can be associated with industrial sources (incineration, paper industry, automobile exhaust, etc.). By assuming that all Na is of marine origin, we have to suppose generally a depletion of Cl^- in particles, as a consequence of chemical reactions of NaCl with HNO_3 and H_2SO_4 (Eriksson, 1959).

Previous results show that the depletion of Cl^- occurs, first of all, in submicron particles and in regions with significant anthropogenic contributions (Martens et al., 1973; Sadasivan, 1978; Patterson et al., 1980).

Table 2
Ratios of ion concentrations with respect to Na^+ (mass/mass) in cloudwater collected during cloud events

Sample	Cl^-/Na^+	SO_4^{2-}/Na^+	K^+/Na^+	Ca^{2+}/Na^+	Mg^{2+}/Na^+
1	1.56	1.80	0.24	0.36	0.11
2	1.45	0.75	0.10	0.23	0.08
3	1.01	0.88	0.22	0.43	0.08
4	1.44	8.27	0.29	0.36	0.12
5	1.93	9.23	0.11	0.32	0.11
6	1.42	8.78	0.21	0.47	0.14
7	1.41	12.95	0.44	0.79	0.14
8	1.17	12.66	0.42	1.30	0.22
9	0.74	1.70	0.29	0.69	0.12
10	1.76	0.60	0.07	0.05	0.11
11	1.64	1.16	0.06	0.10	0.12
12	1.72	1.57	0.16	0.15	0.11
13	1.77	4.41	0.12	0.37	0.13
14	1.60	14.38	0.21	0.89	0.15
15	1.44	9.64	0.42	1.53	0.19
16	1.58	4.62	0.13	0.38	0.15
17	1.35	7.05	1.52	1.73	0.18
18	1.74	3.90	0.16	0.20	0.10
19	1.26	4.24	0.17	0.19	0.10
20	1.31	2.66	0.12	0.18	0.06

As regards to the SO_4^{2-}/Na^+ ratio, which is always higher than the seawater ratio (from 2 to 60 times), it is clear that most sulphate is not of marine origin. The excess of sulphate, that is, nss-SO_4^{2-}, may be calculated from total sulphate using the equation:

$$\left[nss - SO_4^{2-}\right] = \left[SO_4^{2-}\right] - 0.25\left[Na^+\right]$$

where 0.25 is the mass ratio SO_4^{2-}/Na^+ in the seawater.

Sulphate from sea salt to total sulphate ratio is in the range from 2% to 41% in the Vallombrosa samples.

The K^+/Na^+ ratio is always higher than seawater. The K^+ excess can have different explanations. Winkler (1975) and Meinert and Winchester (1977) found anomalously high K^+ concentrations on particles with $r \leq 0.2$ μm over the North Atlantic. This additional K^+ on the small particles may have been from the ocean, resulting from chemical fractionation processes during bubble bursting. Buat-Menard et al. (1974) did suggest that there might be significant fractionation of K^+ as a result of association of K^+ with surface active organic substances in productive waters. Hoffman and Duce (1977) found no enrichment of K^+, Ca^{2+} and Mg^{2+} in atmospheric particles in experiments with Sargasso seawater (low organic carbon) and Narragansett Bay seawater (high organic content). K^+ and Mg^{2+} were enriched in the small particles only with the addition of natural surfactants (extracts of fulvic and humic acid).

Oppo et al. (1999), in an experiment carried out on seawater sampled near the marine station in Leghorn, found negligible enrichment for K^+, Ca^{2+} and Mg^{2+}. In addition, K^+ is a major constituent of fertilizers and is generally present in windblown soil. Vegetation

is another possible source for K^+. Soluble fraction of K^+ in dust is about $1-2\%$ (Chesselet et al., 1972).

Considering the Ca^{2+}/Na^+ ratio, we observed that it is much higher than the seawater one. Ca^{2+} can derive also from crustal aerosol (carbonate and silicate soil mineral) or anthropogenic activity (fertilizers, cement works). This ion contributes from 2.5% to 20% of the total concentration in the examined events.

As regards to Mg^{2+}/Na^+ ratio, it is about equal to the seawater ratio for about 50% of the samples. For Mg, the primary source should be marine and the secondary one could be crustal.

The Ca^{2+}/Na^+, Mg^{2+}/Na^+, K^+/Na^+ and SO_4^{2-}/Na^+ ratios show a similar trend. The significant amounts of Ca^{2+}, Mg^{2+}, K^+ and SO_4^{2-} are thought to be closely linked to the source of surface soil uptake into clouds by orographic lifting mechanisms.

3.1.3. Trace metals

The concentrations in Table 3 represent the soluble (or dissolved) fraction of the reported elements in the liquid phase (cloud droplets). The values in micrograms per air cubic meter (STP: 1 atm, 273 K) are obtained from:

$$X(\mu g\ m^{-3}) = X(\mu g\ l^{-1})LWC(l\ m^{-3})$$

Trace elements can derive from crustal dust, directly from anthropogenic activity (industrial high-temperature processes and traffic) or recycled in marine aerosol during the bursting of bubbles at the wave crests, after deposition on the sea surface. In fact, many natural and man-made surfactants do not have a homogeneous distribution in seawater, but spontaneously segregate (adsorb) at the marine water–air interface.

Measurements along the Tyrrhenian Coast (about 100 km from Vallombrosa) evidence an enrichment (60 and 8, respectively) of the anionic synthetic surfactants (detected as MBAS) and of natural surfactants (SFOM) on the sea surface during rough sea conditions with respect to calm sea, and very high EFs for surfactants and heavy metals (Cu, Cd, Pb, Mn, Fe, Al) in the produced aerosol with respect to surface sea water, increasing with decreasing particle diameter. EFs for organic matter and heavy metals relative to Na in seawater are of the order of 10^4 for particles smaller than 1 μm (Cini et al., 1998; Oppo et al., 1999).

As regards to the crustal origin, compounds such as carbonates, hydroxides, sulphides, oxides and silicates are considered "poorly soluble" or insoluble. However, in very dilute solutions such as atmospheric precipitation, the level of solubility of one of these compounds depends on whether or not its molar concentration is below the limiting solubility. Thus, the ratio soluble/insoluble fraction for these elements is highly variable, depending also on the liquid sample pH. In Table 4, estimated metal solubility for a few elements is reported.

In general, elements associated with anthropogenic and marine sources are rather soluble, while elements from crustal sources are more insoluble. Colin et al. (1990) found in precipitation samples that Al and Fe are present in insoluble forms to the extent of about 80%.

As for sources of considered trace elements, Pb, Cu and Cd are prevalently anthropogenic (fuel combustion, incineration, etc.). Fe, Al and Mn can derive from soil dust or

Table 3
Dissolved metal concentrations (μg l^{-1}) in the 20 water samples: values of air concentrations (μg m^{-3}) are also added, as resulting from the corresponding relation (see text)

Sample	Fe		Pb		Cu		Mn		Cd		Al	
	μg l^{-1}	μg m^{-3}	μg l^{-1}	μg m^{-3}	μg l^{-1}	μg m^{-3}	μg l^{-1}	μg m^{-3}	μg l^{-1}	μg m^{-3}	μg l^{-1}	μg m^{-3}
1	101	2.4E-02	35.8	8.6E-03	50.7	1.2E-02	29.4	7.1E-03	1.6	3.9E-04	302.4	7.3E-02
2	44.8	n.d.	29.2	n.d.	43.9	n.d.	21.8	n.d.	0.97	n.d.	282	n.d.
3	41.5	1.0E-02	4.6	4.3E-03	27.5	2.6E-02	16.1	1.5E-02	2.3	2.2E-03	54.2	5.1E-02
4	117.2	3.9E-02	47.6	4.4E-03	54.3	5.0E-03	24.9	2.2E-03	2.8	2.6E-04	254.6	2.3E-02
5	127	2.7E-02	12.9	2.7E-03	23.7	5.0E-03	8.8	1.8E-03	0.97	2.0E-04	182.6	3.8E-02
6	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
7	62.1	2.1E-02	32.4	1.1E-02	19.6	6.6E-03	2.15	7.0E-04	8.6	2.9E-03	124.8	4.2E-02
8	238.3	2.6E-02	73.8	8.0E-03	80	8.7E-03	33.1	3.6E-03	10.5	1.1E-03	137.3	1.5E-02
9	56.4	8.9E-03	11.8	1.9E-03	35.5	5.6E-03	20.8	3.3E-03	1.7	2.7E-04	82.1	1.3E-02
10	82.6	4.5E-03	52.8	2.9E-03	34.3	1.9E-03	14.8	8.0E-04	0.7	3.9E-05	171.7	9.4E-03
11	64.6	7.7E-03	26.4	3.2E-03	26.7	3.2E-03	12.7	1.5E-03	4.7	5.6E-4	124.4	1.5E-02
12	32.1	4.8E-03	12.7	1.9E-03	22.2	3.4E-03	6	9.1E-04	0.5	7.6E-05	72.7	1.1E-02
13	n.d.	n.d.	41.3	3.5E-03	25.4	2.2E-03	20.6	1.7E-03	2.4	2.0E-04	155.4	1.3E-02
14	157.7	3.5E-02	44.7	1.0E-02	51.5	1.2E-02	27.4	6.2E-03	2.7	6.1E-04	310.8	6.9E-02
15	184.7	2.9E-02	20.8	3.3E-03	71.9	1.2E-02	33.8	5.4E-03	1.5	2.4E-04	206.6	3.3E-02
16	95.9	1.7E-02	18.9	3.5E-03	21.7	3.9E-03	12.4	2.3E-03	0.8	1.5E-04	134.6	2.5E-02
17	30.2	6.6E-03	1.9	4.0E-04	30.1	6.6E-03	14.7	3.2E-03	14.7	3.2E-03	18.4	4.1E-03
18	212	1.9E-02	56.9	5.2E-03	51.1	4.7E-03	16.2	1.5E-03	12.4	1.1E-03	389.1	3.6E-03
19	296.2	7.2E-02	23.17	5.7E-03	45.5	1.1E-02	24.1	5.9E-03	8.77	2.1E-03	551.1	1.3E-01
20	300	4.1E-02	25.66	3.5E-03	46.8	6.4E-03	15.1	2.1E-03	4.37	5.9E-04	466.7	6.3E-02

n.d.: no data.

Table 4
Estimated metal solubility (expressed in percentage) in rainwater and cloudwater

Element	a	b	c	d	e	f	g	h
Al	18	5	26	19	9–20	4–90		
Fe			17	11		0–40	10	
Mn	64			63		54–98		83
Cu	27			71	48–84			
Pb				52	50–90			74
Zn			95		72–96	51–100	95	89
Cd								81

a, Jickells et al. (1992); b, Prospero et al. (1987); c, Colin et al. (1990); d, Guieu et al. (1991); e, Lim et al. (1994); f, Heaton et al. (1990); g, Dutkiewicz et al. (1992); h, Lindberg and Harris (1983).

anthropogenic activity (metal processing, fly ash from oil and coal-fired power plants, exhaust of combustion engines, etc.). Due to the high concentrations measured, we suppose that they are prevalently and directly from anthropogenic activity.

Little information is available on concentrations of trace elements in cloudwater.

Reported data are higher than those found in previous research at high elevation. In fact, Khwaja et al. (1995) at Whiteface Mountain (1512 m asl), a rural site located in the northeastern United States, measured a total concentration (soluble and insoluble) for Fe, Al, Mn, Pb and Cu, of 31, 30, 13, 8 and 4 $\mu g\ l^{-1}$, respectively. Kroll and Winkler (1990) measured in fog water at high elevation (prealpine region) 77 $\mu g\ l^{-1}$ for Pb and 5 μgl^{-1} for Mn. Jickells et al. (1992), in snow samples collected throughout a season at a high altitude (1080 m) site in the Scottish Highlands, measured for Al, Cu and Mn a total concentration of 100, 1.2 and 2.2 $\mu g\ l^{-1}$. Plessow et al. (2001) performed cloudwater investigations at Mt. Brocken (Central Germany) and obtained the following median concentrations for Al, Fe, Mn, Cu, Cd and Pb: 85, 134, 7.8, 5.7, 0.28 and 11 $\mu g\ l^{-1}$.

In our samples, Cu, Cd and Pb are highly correlated, suggesting a common anthropogenic source. The measured concentrations are comparable with the values measured during the Po Valley fog experiment at the ground level (Noone et al., 1992).

As regards to the size distribution of aerosol particles, which can be scavenged from cloud droplets, the heavy metals are usually associated with fine particles, as is also the case for MSA found in many samples, while Ca, Cl, Fe, K, Mg and Na are prevalently correlated with particles of diameter >1 μm.

3.2. Meteorology and cloud chemical composition: samples for individual cloud passages

Clouds occurring at Vallombrosa can be associated to frontal systems or formed locally by lifting processes. Pollutant concentrations in gas and liquid phase and interstitial particulate can derive from local or distant pollution sources, which have influenced the air parcel arriving at the Vallombrosa summit. Processes responsible for aerosol scavenging in clouds are nucleation, impaction due to Brownian diffusion, thermo- and diffusiophoresis. Field measurements conducted at Great Dun Fell (850 m asl) and Mt. Kleiner Feldberg (825 m asl), that is, at an elevation comparable with Vallombrosa site, indicate that nucleation is the dominant scavenging mechanism for aerosol particles (Hallberg et al., 1994; Svenningsson et al., 1997).

Concentrations measured in the liquid phase are related to aerosol and gaseous compounds in the interstitial air of clouds, depending on the partition coefficient of each pollutant.

It is useful to consider the concentrations of a chemical compound X in air-equivalent concentration ($\mu g\ m^{-3}$), so that the dissolved trace substance concentration is independent of the amount of condensed water in which the species is dissolved.

Considering only a few events, we attempt to separate anthropogenic, crustal or sea contribution (local or remote), by examining the chemical composition of the liquid phase and meteorological conditions.

3.2.1. Event 1: 10/12 November 1992—Sample 1

Although it includes episodes occurring over a 3-day period, this can be considered as a homogenous event in view of the temporal continuity and meteorological situation.

To value sources of ions present in the cloudwater, we consider the EF for Ca^{2+}, K^{+}, SO_4^{2-} and Mg^{2+} with respect to sea water. The values are 9.5, 7, 7 and 1, respectively. So Ca^{2+}, K^{+} and SO_4^{2-} have other sources in addition to sea. As the almost unitary EF for Mg^{2+} indicates that the origin is only from the sea and not crustal, the other ions considered should have a prevalently anthropogenic origin. As in this sample, the MBAS concentration is high ($\cong 0.23\ \mu g\ m^{-3}$); Fe, Mn, Al and Pb should come not only directly from anthropogenic activity, but could also be reemitted into the atmosphere from seawater during the bursting of bubbles with a high EF, since these cations are able to couple with marine surfactants. EFs relative to Na in seawater, for Al, Pb, Cu, Mn, Fe and Cd, are of the order of 10^5.

Measured concentrations (Table 1a,b) of Na^{+} and Cl^{-} ($\cong 3\ \mu g\ m^{-3}$) and MBAS indicate a significant sea contribution. MBAS carried from river water and joined to human activity is present throughout the Tyrrhenian Sea. In conclusion, sea and anthropogenic contributions should be dominant in this event.

The meteorological analysis appears to confirm this conclusion. Isobaric surface, 850 hPa, shows air mass coming from the west (Atlantic Ocean) and reaching Italy, through France and Spain.

The clouds detected by satellite images are low during the earlier part of the day considered and medium–high at remaining times. They move from north to south along the peninsula carrying an anthropogenic contribution. This explains the marine and anthropogenic components detected by the chemical analyses.

3.2.2. Event 8: 11 June 1993—Sample 8

Anthropogenic elements Pb, Cd and Cu show high concentrations, that is, 8, 8.7 and 1.1 ng m^{-3} (Table 3). The Ca^{2+}, Mg^{2+} and K^{+} concentration ratios with respect to Na^{+} are much higher than those in seawater (Table 1a). For SO_4^{2-}, EF is about 50.

As Cl^{-}/Na^{+} ratio is lower than the seawater value, a Cl^{-} loss occurs by a previously explained mechanism. As the Na^{+} concentration is about 0.53 $\mu g\ m^{-3}$, we can conclude that in this sample, there is, in addition to the anthropogenic and crustal contributions, also a marine one. The 850-hPa chart for 11 June 1993 shows a center of high pressure over the Mediterranean and Atlantic, and a low-pressure center over the UK.

The air mass is therefore moving from the Atlantic over France and Spain, reaching Italy with its marine component. The clouds detected by satellite images during the final part of the sampling are convective in character, so the trajectory analysis at the end of this event could break down. The convection gives rise to a remixing within the lower atmospheric layers, incorporating into the cloud air from the boundary layer. It therefore brings about a local crustal and anthropogenic contribution to the air mass.

3.2.3. Event 11: 15/17 December 1993—Sample 11

Chemical analyses show that Ca^{2+}, Mg^{2+}, K^+ and SO_4^{2-} concentration ratios with respect to Na^+ are slightly higher than those in seawater (Table 2). The EFs are respectively 2.7, 1.1, 1.7 and 4.6. The Al, Fe, Mn and Cu concentrations are relatively low, while those of Pb and Cd are slightly higher (Table 3). The Na concentration is very high, about 1.75 $\mu g\ m^{-3}$. In conclusion, the prevalent contribution should be seawater and to a lesser degree, anthropogenic. The synchronous scan fluorescence spectra for cloudwater, marine water and marine aerosol sampled in Leghorn (Tyrrhenian Sea) show a similar trend, and therefore, further support the marine origin of cloud sample.
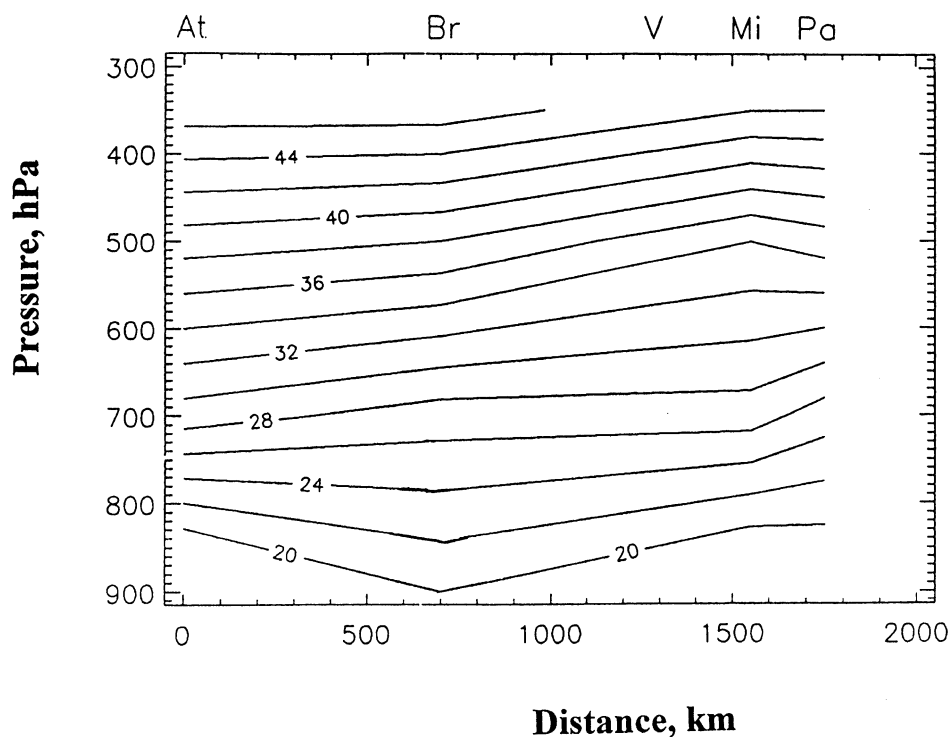

Fig. 7. Isothermopotential diagram for 9 May 1994. At, Athens; Br, Brindisi; Mi, Milan; Pa, Payerne. The position of Vallombrosa site is indicated.

Surface and 850-hPa synoptic charts show a large low-pressure area centered over the UK. For both surfaces, air masses go from west to east and the associated cold front is moving southwards. Therefore, air mass trajectories account for the prevalence of sea components in the considered sample.

3.2.4. Event 15: 9 May 1994—Sample 15

In this sample, Ca^{2+}, K^+ and SO_4^{2-} concentration ratios with respect to Na^+ are much higher than those in seawater (Table 2). The EFs are respectively 40, 11 and 38.

The Al, Fe, Pb, Cu and Mn show high concentrations: 0.033, 0.03, 0.0033, 0.0011 and 0.0054 µg m^{-3} (Table 3). Thus, the prevalent contribution should be anthropogenic and crustal, with a smaller sea contribution ($Na \cong 0.3$ µg m^{-3}).

The surface map reveals a high-pressure zone over the eastern Mediterranean and low pressure over the Tyrrhenian Sea, with an associated front approximately following the 10°E longitude. The circulation rotates around the low-pressure area over Corsica, determining the southerly direction of the clouds passing over Vallombrosa, as shown also by satellite images. Isothermopotential curves show around 850 hPa a lowering and subsequent rise in curves around Vallombrosa (Fig. 7). This explains the crustal and anthropogenic contributions.

4. Summary and conclusions

Cloudwater samples were collected from November 1992 to March 1995 in Vallombrosa, a typical mountain station facing the valley of the Arno, an urbanized and industrialized area strongly affected by air pollution. Inorganic soluble ions (NH_4^+, Ca^{2+}, Mg^{2+}, Na^+, K^+, Cl^-, SO_4^{2-}, NO_3^-, H^+), trace metals (Fe, Pb, Cu, Mn, Cd, Al) and organic components (MBAS, MSA, SFOM) were chemically analyzed.

All examined inorganic soluble ions contributed significantly to the TIC. The region is exposed to significant pollutant levels, influencing the forest disease, as a result of cloud droplet interception and wet deposition.

The TIC ranged from 640 to 7476 µeq l^{-1} and decreased with increasing LWC. The relationship between TIC and LWC based on all considered events is given by: $TIC = aLWC^b$, with $a = 92\,011$ and $b = -0.76$ ($r = 0.73$).

The average concentrations for NH_4^+, NO_3^- and SO_4^{2-} were 364, 468 and 301 µeq l^{-1}, respectively. The ratio between SO_4^{2-} and NO_3^- ranged from 0.92 to 3.46 and was >1 for 86% of the samples. This dominance of sulphate over nitrate indicates that SO_4^{2-} primarily contributed to the acidity of cloudwater. As abundant traces of MAS were found in the examined samples, we deduce that an additional source of sulphate is from oxidation of DMS released by the biogenic activity on the marine surfaces. The pH was between 3.21 and 6.22. The NH_4^+ concentration is well correlated with the sum of $NO_3^- + SO_4^{2-}$. This indicates that ammonium sulphate and nitrate aerosols contribute to a large fraction of these anions.

Soluble fractions of Fe, Pb, Cu, Mn, Cd and Al are higher than those found in previous studies at high elevation. In our samples, Cu, Cd and Pb are highly correlated, suggesting a common anthropogenic source.

Soluble trace metals can derive from crustal dust, directly from anthropogenic activity or recycled in marine aerosol during the bursting of bubbles at the wave crest, after deposition on the sea surface. In fact, SOM (both natural and man-made) present in the seawater, greatly increases in concentration due to adsorption when bubbles are formed on the sea surface. The spray of prevalently submicron droplets produced from the bursting of the bubble cup shows a high EF not only for SOM, but also for heavy metals, which interact with SOM. Thus, heavy metals can be present in cloud droplets even if the air mass is purely of marine origin.

Chemical and meteorological analyses reveal that a marine source is always present, often with a crustal and/or anthropogenic one. The relative abundance of MBAS with respect to marine salts could explain the damage to Vallombrosa vegetation, as droplets distribute a continuous liquid film and wash the wax on the leaf surface, so favouring the penetration of pollutants through the stomata. Natural surfactants (e.g. humic substances) do not show detergent property, so the damage to vegetation is due only to pollutants (e.g. heavy metals) interacting with them.

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