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Publisher *Taylor & Francis*

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International Journal of Environmental Analytical Chemistry

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713640455>

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To cite this Article Mangoni, Monica , Udisti, Roberto and Piccardi, Giovanni(1998) 'Sequential Sampling of Rain: Construction and Operation of an Automatic Wet-Only Apparatus', *International Journal of Environmental Analytical Chemistry*, 69: 1, 53 – 66

To link to this Article: DOI: 10.1080/03067319808032574

URL: <http://dx.doi.org/10.1080/03067319808032574>

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SEQUENTIAL SAMPLING OF RAIN: CONSTRUCTION AND OPERATION OF AN AUTOMATIC WET-ONLY APPARATUS

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(Received 28 January 1997; In final form 11 July 1997)

An automatic wet only sequential sampler able to divide rain events in fractions <0,1 mm was developed in order to point out the scavenging influence on the rain composition. In this apparatus special pinch solenoid valves have been used to avoid contact between the mechanical parts and the rain sampled. The rain is collected by volume and, since the sampler is connected to a timer able to memorize the exact time of sampling tube changes, it is possible to calculate the rain intensity as well.

The collected rain is then analysed by ion chromatography to obtain the concentrations of inorganic and some organic anions.

Preliminary results for some events collected in the centre of Florence are also reported and the differences in the time series of some components are explained by meteorological considerations.

Keywords: Rainwater collector; sequential sampling; chemical composition; precipitation scavenging

INTRODUCTION

The analysis of atmospheric depositions is a good way to study the tropospheric aerosol composition and the removal phenomena of natural and anthropogenic substances.

The first method for studying and analysing atmospheric depositions was the indiscriminate collection of all atmospheric depositions over certain periods.

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This technique requires only simple devices, but is not able to discriminate between wet and dry depositions. An important improvement is the use of samplers capable of separating dry depositions from rain collection. These collectors are fitted with a rain detector that determines the opening of a wet-only deposition bucket at the beginning of the rain event.

A single rain event can be collected and stored separately, but to establish a unique criterion for distinguishing two successive rain events has been a problem for the teams working on individual events^[1]. Moreover, rapid variations in precipitation composition are smoothed for long period events^[2]. The infra-storm variability can be studied by dividing a rain water event into sub samples with an appropriate resolution. According to Asman^[3] this variability can be wide: he showed that the chemical composition of the first 0.5 mm of precipitation can exceed the average composition by a factor of 50.

In a recent review Laquer^[4] considers various reports concerning the construction and use of rain sequential samplers.

The rain may be fractionated by volume or at uniform time intervals; time-based samplers are much simpler to develop and operate but, if the time between two samples is short and rain intensity is low, the water collected in each tube can be insufficient for chemical analysis. On the other hand, in high intensity rain events, tubes can easily overflow. In the case of storm events with high variable intensity, such as precipitation in temperate regions, there is a high risk of miscalculated data. Collectors at constant volumes are generally more complex, but they can easily handle both high and low intensity rain events^[5]. Automatic sequential precipitation samplers can be dependant on an external source of power or not. In the latter case the apparatus may also be used in remote sites, but generally the fractionating range is wider than those realised by a power-dependant sampler and thus less information concerning the internal variation of the rain is obtained^[6, 7].

The principal disadvantage of a volume-based power-dependant fraction collector is the necessity to have the volume gauge in contact with the sample and this can be a primary source of contamination.

For this reason an automatic power-dependant sequential sampler in which the sample does not touch the mechanical part has been designed and realised. The structure and functioning of the sampler and its application to rain in Florence are reported.

MATERIALS AND METHODS

Sampling

The sampler was based on a modified “wet and dry” sampler (MTX mod. ARS 1000 Bologna-Italy) having a rain detector that controls the movements of a cover from the wet to the dry bucket avoiding the dry deposition before the onset of the rainfall.

The wet bucket of this sampler was substituted by a polyethylene funnel with an internal diameter of 29.5 cm. corresponding to a sampling area of 683 cm². The outlet of the funnel is connected to a silicon tube by means of a glass funnel.

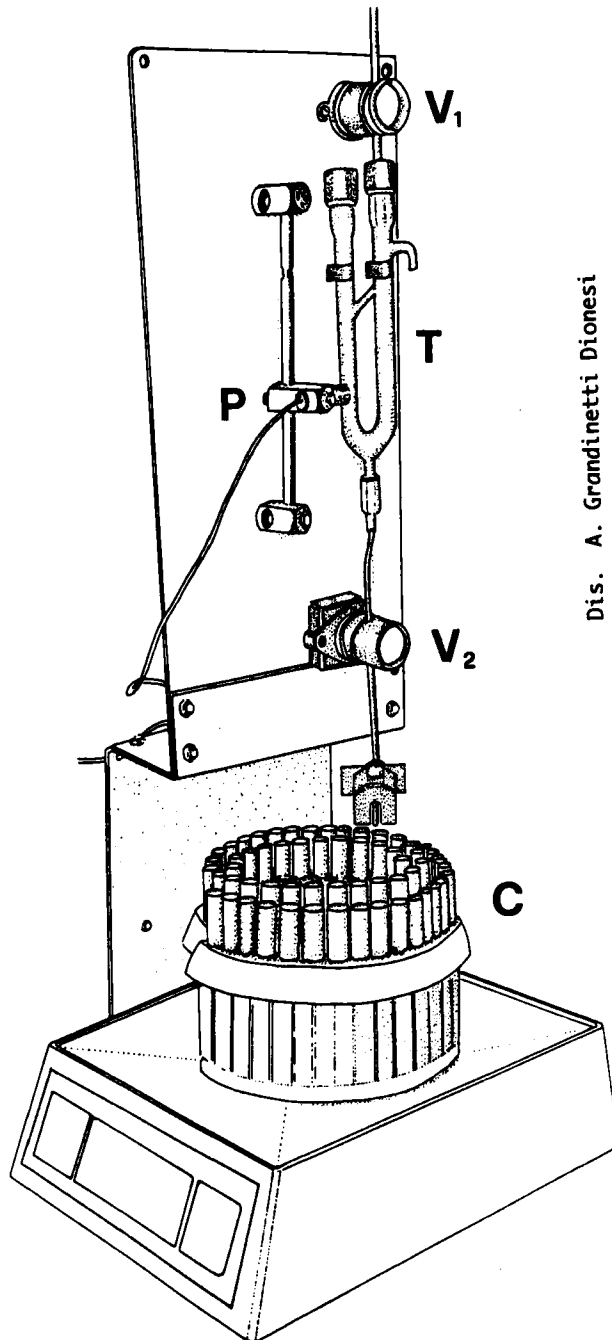
A normally open pinch solenoid valve (V1 in Figure 1—Sirai, Italy) is placed on this silicon tube that is connected to one arm of a Y glass tube (T). An inductive proximity probe (P-Rechner, W-Germany) is situated on the second arm of the Y tube. The probe can slide vertically to change the level of water in the Y tube with a consequent major or minor rain-event subdivision.

The lower arm of the Y tube is connected to the carousel of the fraction collector by means of a silicon tube on a normally closed pinch solenoid valve (V2). The carousel (C) of the fraction collector (Bio-Rad, mod. 2110 Fraction Collector) can contain 80 12 mL tubes. Considering the area of the funnel, this apparatus can collect 14 mm of rain divided into 80 fractions of max 0.18 mm. The opening and closing of the valves and the movement of the carousel are determined from a small electronic station which receives the starting impulse from the probe (P). The fraction reproducibility of this system is about 5%.

During the sampling valve V2 is closed and V1 is open; therefore the rain water accumulates contemporaneously in the two arms of the Y glass tube. The use of a double vertical tube avoids accidental rain drops being read by the probe.

When the water level reaches the position of the probe, this through the electronic station closes the valve V1 and opens the valve V2 so that only the rain fraction just collected in the Y tube is transferred into the collection tube. The time necessary for emptying the Y tube is about 5 seconds and after this time the electronic station inverts the status of these two valves so that collection of the next fraction is possible. At this time the electronic station shifts the carousel C one position, so that a new tube is ready to collect the next fraction.

Silicon tubes, glass funnel and fraction tubes were accurately cleaned and the contamination level for all the studied components was periodically checked. All the devices used for rain sampling were maintained in two sealed plastic bags at cold and dark. Before sampling they were washed with UHQ water and were placed in the collecting position.



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FIGURE 1 Sequential rain sampler with fraction collector.

After collection, the samples were kept at +4°C. When sampling was conducted at night the rain fractions were collected the following morning. This delay did not cause any decrease in the concentration of organic anions. Herlihy and co-workers^[8] have verified that significant bacterial activity could be measured if samples were incubated at room temperature for at least two days. We, too, verified the absence of the micro-organisms activity by collecting a bulk rain event and dividing it into various sub-samples. Three of these sub-samples were immediately analysed and three were analysed being left uncovered outdoors for 24 hours. No significant decrease for acetates or formates was observed. Analysis was performed the day after sampling. Immediately before analysis the samples were weighed and filtered on an 0.45 µm pre-washed Teflon membrane filter.

The ion chromatographic measurements were performed on a Dionex 4000i Ion Chromatographic System, CDM-1 Conductivity Meter and a Data Processing System using the Autoion 450 software.

The determinations of inorganic (Cl^- , NO_3^- , SO_4^{2-} , F^-) and organic (acetates, formates, pyruvates and methanesulphonates) anions were performed by the method described by Udisti et al.^[9]. The organic anions and fluoride were separated using a Dionex AS5A column with a isocratic elution (eluent: Na tetraborate); the inorganic anions were determined on a Dionex AS4A column with a carbonate/bicarbonate eluent^[10].

For the ion chromatographic determination of the inorganic and some of the organic anions about 5 ml of sample was necessary; a fraction volume of 7 ml, equivalent to 0.1 mm of rain, was chosen as a fair compromise between the analytical requirement and the necessity to obtain a good rain fractionation. The mean intensity of rainfall in Florence, during the period of sampling was about 0.5 mm/min; since our apparatus can collect a maximum intensity of 1.2 mm/min it was able to sample the majority of the precipitation events without fraction mixing.

RESULTS AND DISCUSSION

The sampling site was the Botanical Garden of the University of Florence situated in the town-centre, where the anthropogenic contribution to local aerosol composition can be significant. This location was also selected for its nearness to the analytical laboratory to avoid transporting the samples and the chloroform addition necessary to prevent the bacterial growth on the organic compounds^[11]. In fact chloroform can produce a formate contamination (Hartmann, personal communication, 1992).

Four rain events were collected in 1992 for instrument testing and to check the performance of the system for the study of scavenging phenomena.

Figure 2 shows the four box-plots for Cl^- , NO_3^- and SO_4^{2-} for the collected events that appear of different behaviour. A high concentration of the three components is observed at the beginning of the rains on 31/3 and 3/12 and these values decrease with time. This phenomenon is not observed in the February precipitations and concentrations are distributed in proximity of the median value. The different behaviour of the February rain is due to the vicinity of previous events that reduced the accumulated aerosols from the atmosphere.

Considering all samples, a good correlation ($r = 0.94$) between nitrate and sulphate is observed as shown in Figure 3. The median value of the weight ratio

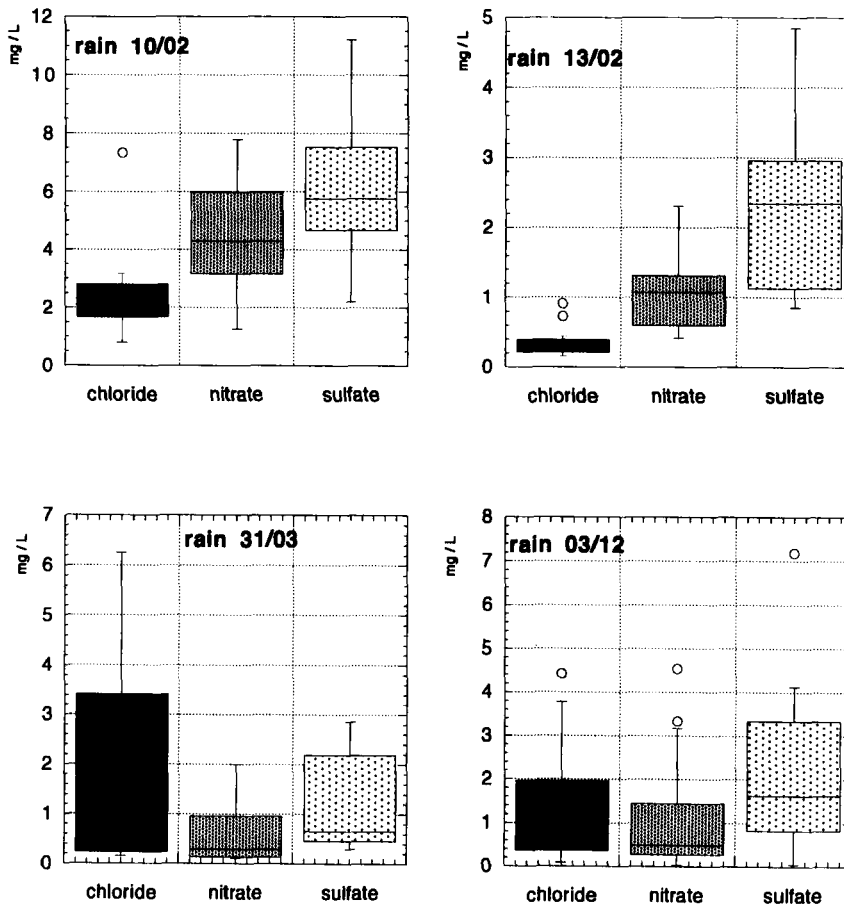


FIGURE 2 Distribution per-event deposition of chloride, sulfate and nitrate.

SO₄/NO₃ is 1.86 but, for each sample, this ratio changes greatly during the rain. The ratio value is a little higher than the 1.68 found by Udisti et al.^[12] in the rains collected in Florence with a traditional wet only apparatus and is analogous to the 1.8 found by Zilio Grandi et al.^[13] in the Venice regional network (Italy) and by Church et al.^[14] in the northern Atlantic. Higher values, 2.27 and 2.21, have been obtained by Pellet et al.^[15] and by Asman et al.^[16] respectively in U.S.A. using a sequential sampler.

Significant variations in concentration may be observed during the rain events; in fact, in addition to the concentration decreases in the first fractions previously described, peaks of concentration are noted for some components. The time series of the 31/3 event in Figure 4 shows this phenomenon. In this figure, to better evidence the composition variation of the four components, % of concentration deviation from the mean (indicated as delta) versus the cumulative mm of rainfall is shown. This value is obtained:

$$\text{delta \%} = 100 (x - X)/X$$

where x is the measured concentration of each sample and X is the mean concentration of the whole event. In this case a similar behaviour for sulphate,

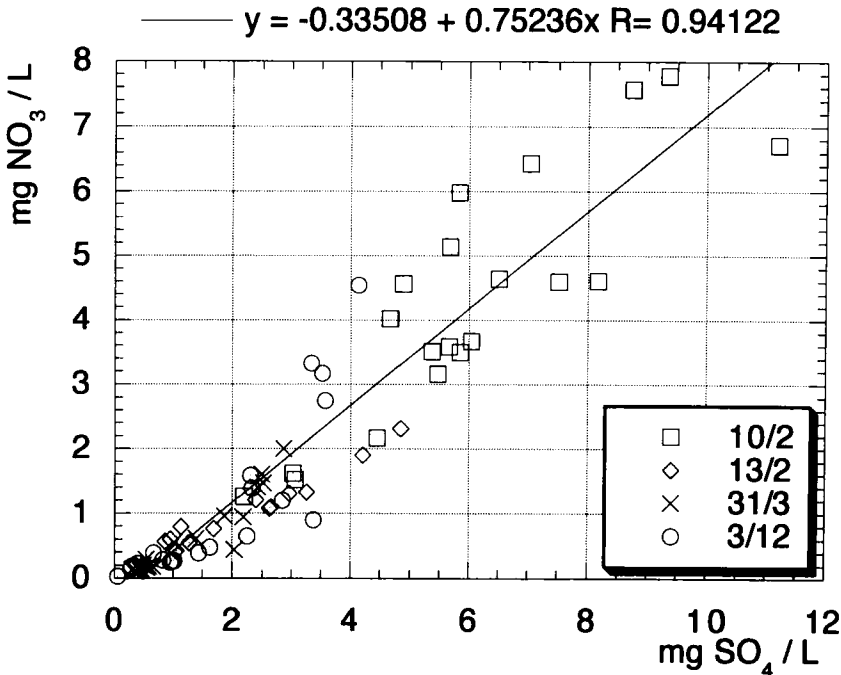


FIGURE 3 Relationship between nitrate and sulfate concentrations of all events considered.

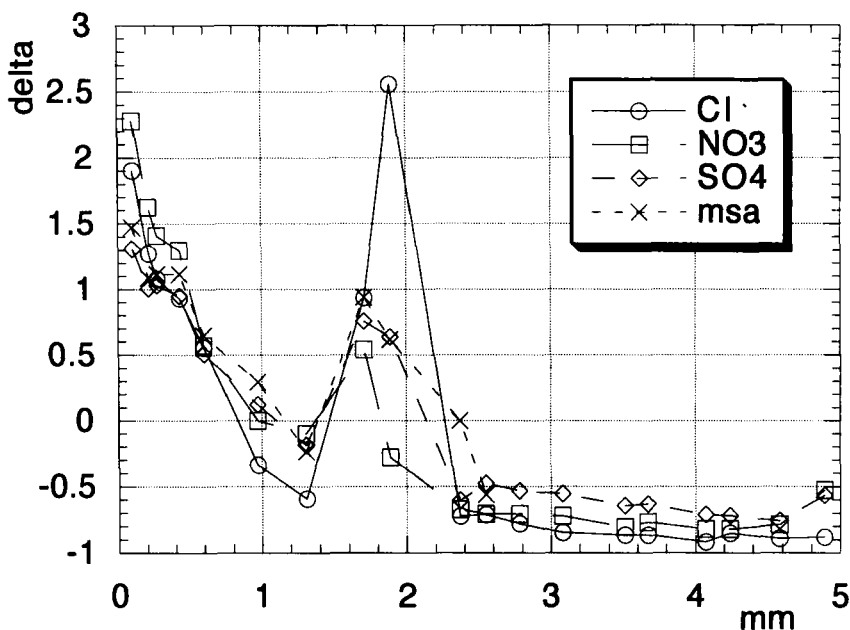


FIGURE 4 Variations in quality of the 31/03 rainfall.

chloride, nitrate and methanesulphonate is observed. An analogous behaviour is observed for the event of 13/2 with the concentration maximum of the same four components that appear at 3.5 mm of rain.

In both events the concentrations of formate and acetate, on the contrary, decrease continuously from the beginning of the rain indicating a different origin or removal processes for both components. For the 03/12 rain event the time series reveal two different periods. In the first one (<2.5 mm) peaks of concentration for chloride, nitrate and sulfate are observed but not contemporaneously as in Figure 4; while in the second period a uniform decrease in concentration values is recorded. This diverse behaviour corresponds to a sudden variation of rain intensity that passes from <0.1 to about 0.8 mm/min. The effect of this variation at 2.5 mm of rain is better observed in Figure 5 which shows the correlation between nitrate and sulphate (A) and between nitrate and chloride (B). The samples collected before 2.5 mm (low intensity) are indicated as empty circles and are connected by segments in order of their collection. In the same figures the samples >2.5 mm are indicated as triangles and the dotted line indicates the linear regression with $R = 0.96$ for A and $R = 0.98$ for B. The mean value of the $\text{SO}_4^{2-}/\text{NO}_3^-$ weight ratio in the second period of the precipitation, where apparently the wash-out process is strongly reduced, is 2.95. The triangles

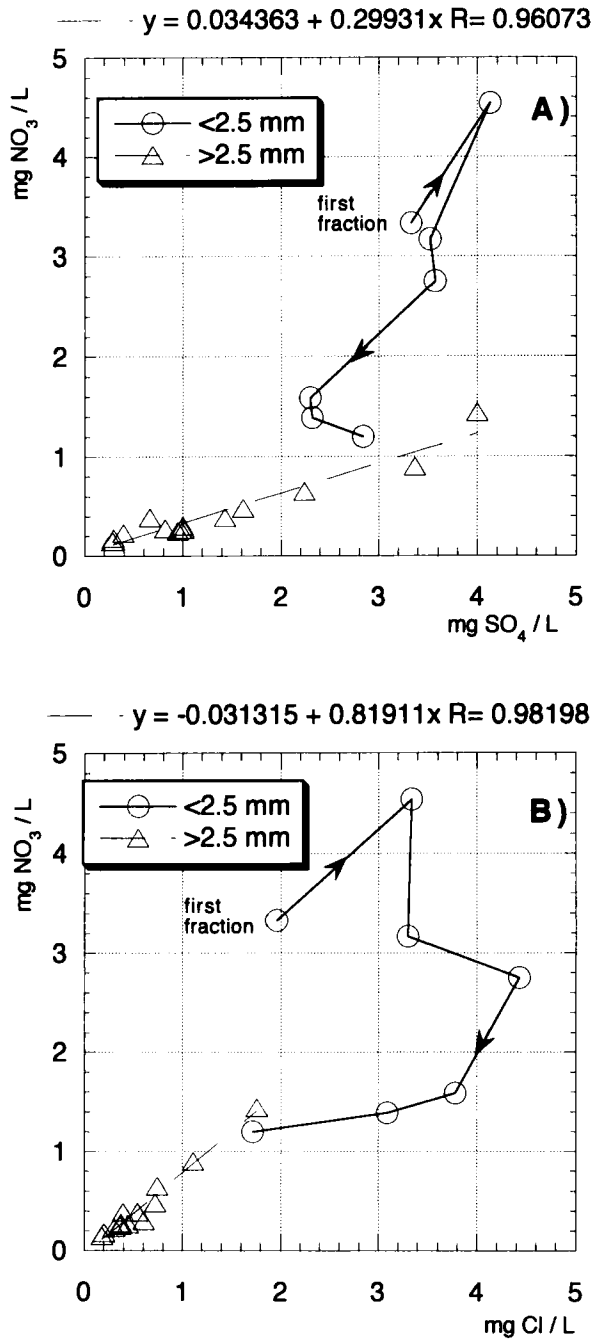


FIGURE 5 Relationships between nitrate and sulfate (A) and nitrate and chloride (B) for the 03/12 rain event.

of Figure 5 are aligned in order of collection and show a decrease in concentration for SO_4^{2-} , Cl^- and NO_3^- . The constant ratios $\text{NO}_3^-/\text{SO}_4^{2-}$ and $\text{NO}_3^-/\text{Cl}^-$ might possibly be due to a progressive dilution of a constant composition reserve.

The city of Florence is not far from the Tyrrhenian sea (about 70 Km) and it can be hypothesized that some components of marine origin are found in the rain because many rain events are produced by disturbances coming from the west. Chlorides and methanesulphonates (MSA) may be considered the most indicatives of a marine contribution to the rain. We cannot exclude an anthropogenic contribution of chlorides but supposing that all Cl^- is of marine origin we can obtain the nssSO_4^{2-} concentration that represents the biogenic and anthropogenic contribution of sulphates. Figure 6 shows the concentrations of nssSO_4^{2-} and of msa for both events of 13.2 and 31.3 and the points are well aligned ($r > 0.94$) on two regression lines with analogous slopes. The mean value of the $\text{nssSO}_4^{2-}/\text{MSA}$ ratio (w/w) of both events is 217. This value is near the one (about 200) found in the aerosol sampled in the meteomarine station of Leghorn⁽¹⁷⁾ in conditions of marine winds at low velocity.

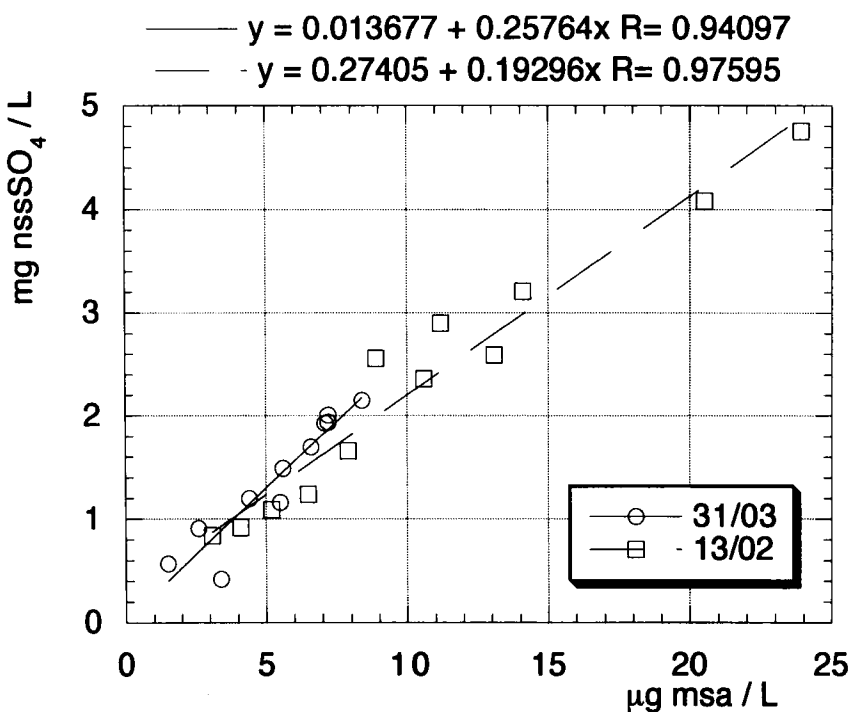


FIGURE 6 nss-Sulfate versus msa concentration plot for 13/02 and 31/03 rain events.

The box plots calculated from acetate and formate concentrations of all sampled events are shown in Figure 7. In an analogous manner to the three inorganic anions both organic acids show median values in the centre of the box for both February precipitations during which there is no decrease in concentration at the beginning. On the contrary the other two precipitations show a decreasing of acetate and formate concentrations during the event that is evidenced by the position of median in the box-plot in Figure 7.

Figure 8 shows the concentrations of acetate and formate of all four events collected with the sequential rainfall sampler; the points are aligned, with a good correlation coefficient ($R = 0.931$), along the empirical polynomial curve $[Fo] = 22.1 + 0.504 [Ac] - 7.46 \cdot 10^{-5} [Ac]^2$. In the four events considered the mean

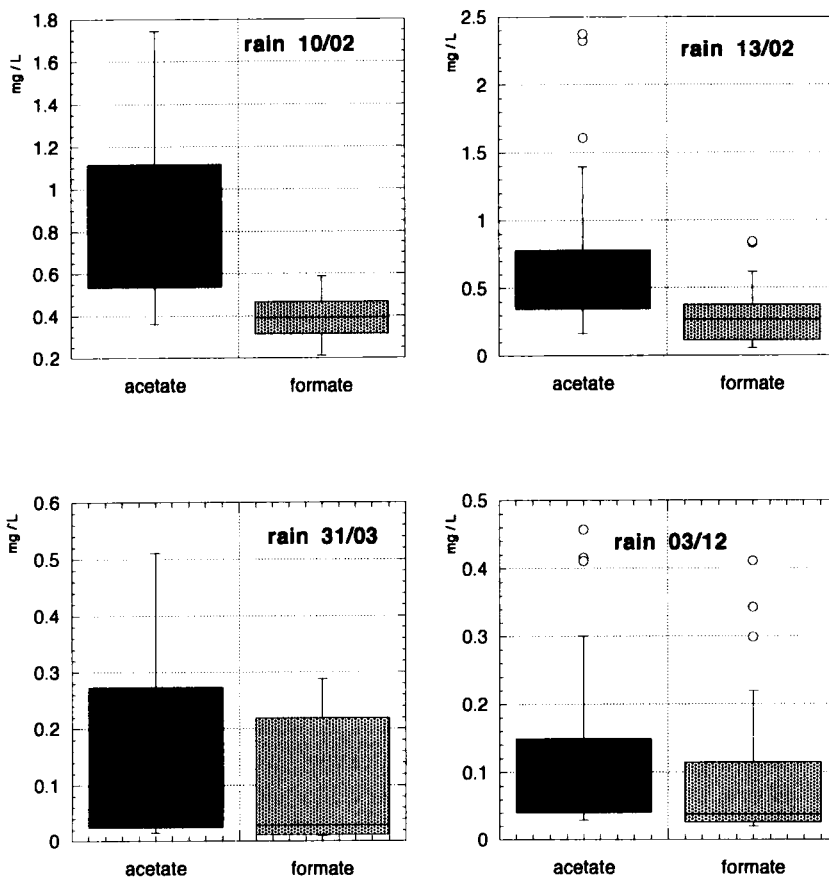


FIGURE 7 Distribution per event deposition of acetate and formate.

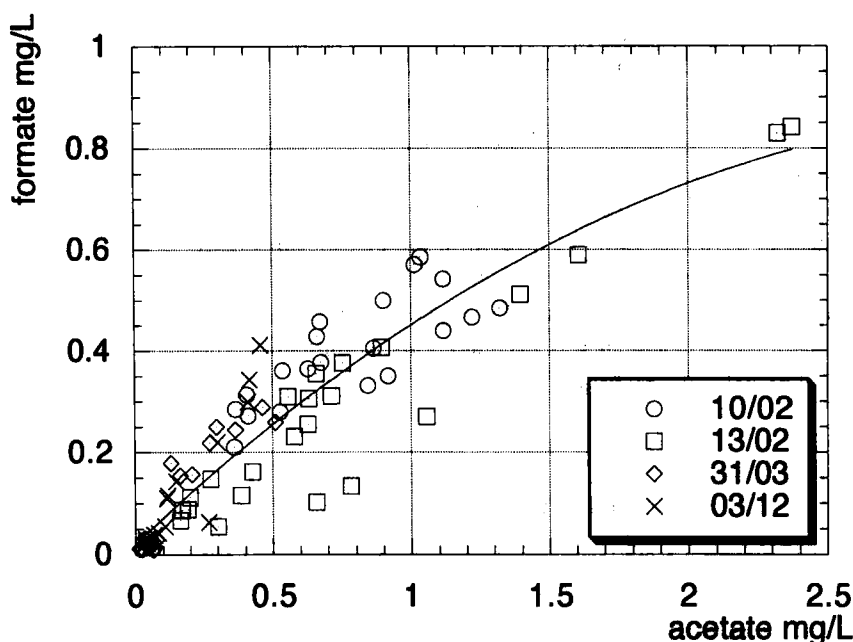


FIGURE 8 Relationship between acetate and formate for all events.

value of the ratio Ac/Fo is 2.47 apparently due to the source dominated sample caused the town pollution.

In fact Hartmann *et al.*^[18] found that the ratio acetates/formates measured in a scrub-grass savanna and in a near by semideciduous forest (in situ formation) is, for most of the time, less than one. Grosjean^[19], with measurements from automobile exhausts and in highway tunnels, on the contrary showed higher emissions of acetic acid with an acetate/formate ratio of 4.3 and 2.6, respectively. Successively, Grosjean^[20] estimated emission rates, in situ formation rates and removal rates by dry deposition concluding that at the source dominated site the ratio Ac/Fo is about 2.1-2.3 while where in situ formation dominates this ratio is $\ll 1$. The different acetate concentration slope may be caused by different solubility conditions of both components. In fact the partitioning of formic acid and acetic acid between the liquid and gaseous phase in the atmosphere depends on the amount of liquid water^[21]. At low water contents formic acid is dissolved first and this can explain why enriched formic acid is more frequently found than acetic acid.

The majority of samples contain determinable quantities of pyruvates. The difference of behaviour between the February samples and the others is also shown for this component. In fact, while pyruvates are present in all samples

collected in February in a concentration range of 10-90 $\mu\text{g/L}$, in the 31/03 and 03/12 events only 16% and 54% of samples, respectively, show a concentration higher than the detection limit (0.4 $\mu\text{g/L}$). In the February samples a modest correlation between pyruvate and acetate ($R = 0.659$) and pyruvate and formate ($R = 0.595$) can be found. The presence of pyruvates in aerosols, and consequently in rain, is probably due to a radical oxidation of hydrocarbons. Jacob and Wofsy^[22] have suggested that pyruvic acid is produced by the gas-phase oxidation of vegetal origin isoprene.

Andreae et al.^[23], from the analysis of rains collected in 1985 at Manaus (Brazil) and in 1986 at Tallahassee (Florida) found that pyruvate was detectable in all rain samples in a range of 7.9-109 and 3.5-229 $\mu\text{g/L}$ respectively. Andreae et al.^[24] later observed that in precipitations in central Amazonia, pyruvate was present at concentrations of 2.6-82.8 $\mu\text{g/L}$ with a strong correlation ($R = 0.78$) to formates. The formate/pyruvate weight ratios based on the regression slopes for all data are 12.2 (Manaus + Tallahassee) and 11.9 (Central Amazonia). The same ratio, obtained as a mean value of ratios of the single samples collected in Florence is 11.3 with a minimum difference of values for each event.

CONCLUSIONS

An automatic sequential sampler has been built and used to collect 0.1 mm rain fractions. The volume of obtained samples is sufficient to determine inorganic and some organic anions by ion chromatography and then to obtain concentration profiles during rainfall events.

The results show that the concentrations of the various chemical components can vary in a complicated manner within a single rainfall. Different events show different behaviours but a statistical elaboration of all data indicates a high correlation between sulphates and nitrates. In single events some significant correlations have been seen between different components.

The study of the causes of these variations can lead to a better comprehension of the removal processes of the gases and aerosols incorporated in rain water.

References

- [1] J. L. Jaffrezo and J. L. Colin, *Environ Technol Letters*, **8**, 467-474 (1987).
- [2] F. C. Laquer, *Chemosphere*, **20**, 277-285 (1990).
- [3] W. A. H. Asman, *Water, Air and Soil Pollut.*, **13**, 235-245 (1980).
- [4] F. C. Laquer, *Atmos. Environ.*, **24A**, 2289-2297 (1990).
- [5] L. Poissant and P. Beron, *Water Resources*, **26**, 547-551 (1992).
- [6] D. B. Wyk and W. D. Stooch, *Water (SA)*, **17**, 183-187 (1991).
- [7] R. Udisti and F. Casella, *Ann. Chim. (Rome)*, **84**, 113-128 (1994).
- [8] L. J. Hertlhy, J. N. Galloway and A. L. Mills, *Atmos. Environ.*, **13**, 2397-2402 (1987).

- [9] R. Udisti, S. Bellandi and G. Piccardi, *Fresenius J. Anal. Chem.*, **349**, 289-293 (1994).
- [10] G. Piccardi, R. Udisti and E. Barbolani, *Ann. Chim. (Rome)*, **79**, 701-712 (1989).
- [11] W. C. Keene and J. N. Galloway, *Atmos Environ*, **18**, 2491-2497 (1986).
- [12] R. Udisti, S. Bellandi, S. Del Panta, E. Barbolani and F. Pantani, *Ann. Chim. (Rome)*, **83**, 223-232 (1993).
- [13] F. Zilio Grandi and L. Szpyrkowicz, *Fresenius J. Anal. Chem.*, **341**, 625-630 (1991).
- [14] T. M. Church, J. M. Tramontano, D. M. Whelpdale, M. O. Andreae, J. N. Galloway, W. C. Keene, A. H. Knap and J. Tokos, *J. Geophys. Res.*, **96D**, 18705-18725 (1991).
- [15] G. L. Pellet, R. Bustin and R. C. Harriss, *Water, Air and Soil Pollut*, **21**, 33-49 (1984).
- [16] W. A. H. Asman, P. Jonker, J. Slanina and J. H. Baard, *Precipitation, Scavenging, Dry Deposition, and Resuspension*, (H. R. Pruppacher et al. eds. Elsevier, 1983), vol 1, pp 265-274.
- [17] E. Schiavuta, P. Mittner and R. Cini, *Il monitoraggio automatico dell' inquinamento marino*. (CNR-SCI Workshop proceedings, Taranto, Italy, April 1992), pp 313-330.
- [18] W. R. Hartmann, M. Santana, M. Hermoso, M. O. Andreae and E. Sanhueza, *J. Atmos. Chem.*, **13**, 63-72 (1991).
- [19] D. Grosjean, *Environ. Sci. Technol.*, **23**, 1506-1514 (1989).
- [20] D. Grosjean, *Atmos. Environ.*, **26A**, 3279-3286 (1992).
- [21] G. Helas, M. O. Andreae and W. R. Hartmann, *J. Atmos. Chem.*, **15**, 101-115 (1992).
- [22] D. J. Jacob and F. C. Wofsy, *J. Geophys. Res.*, **93**, 1477-1486 (1988).
- [23] M. O. Andreae, R. W. Talbot and Shao-Meng Li, *J. Geophys. Res.*, **92D**, 6635-6641 (1987).
- [24] M. O. Andreae, R. W. Talbot, H. Berresheim and K. M. Beecher, *J. Geophys. Res.*, **95D**, 16987-16999 (1990).