

## Red rains as major contributors of nutrients and alkalinity to terrestrial ecosystems at Montseny (NE Spain)

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**Abstract.** During two years (1983-1985), 8 red rains were collected in the Montseny mountains. The suspended matter contained in red rains has its source in the Sahara desert and corresponds to fine silts. Due to the calcite content of dust responsible for the red rains, these rains are alkaline with a volume weighted mean pH of 7.7 versus 4.7 of non-red rains. Estimated  $\text{HCO}_3^-$  alkalinity input due to red rains is 0.21 keq/ha/yr and total annual  $\text{HCO}_3^-$  alkalinity input is 0.24 keq/ha/yr. To that figure, one has to add at least 0.24 keq/ha/yr due to the alkalinity of calcite contained in red dust. For the same period, hydrogen input in bulk deposition amounts to 0.19 keq/ha/yr. These results indicate that acidity due to non-red rain episodes is neutralized on an annual basis, with red rains being the major neutralizing agent. Ion concentrations in red rains are high, which makes them an important source of nutrients even though they only account for 5.4% of annual precipitation. Red rains are particularly enriched with  $\text{Ca}^{2+}$  having a volume-weighted mean  $\text{Ca}^{2+}$  concentration 14 times higher than non-red rains and delivering 46% of the annual inputs of soluble  $\text{Ca}^{2+}$  in bulk precipitation at Montseny.

**Resum.** *Paper de les pluges de fang en l'aport atmosfèric de nutrients i d'alcalinitat al Montseny.* Durant dos anys (1983-1985) es varen recollir 8 pluges de fang a La Castanya (Montseny). La matèria particulada de les pluges de fang s'origina al desert del Sahara, i correspon a llims fins. Degut al contingut de calcita d'aquests llims, les pluges de fang són alcalines, amb un pH mig de 7.7, enfront de 4.7 per la resta de les pluges. L'entrada anual estimada d'alcalinitat en forma de bicarbonat dissolt a les pluges de fang és de 0.21 keq/ha/any, d'un total estimat de 0.24 keq/ha/any per totes les pluges. A aquesta xifra cal afegir almenys 0.24 keq/ha/any degut al contingut de calcita a la fase sòlida de les pluges de fang. Durant el mateix període, l'entrada d'hidrogenions a la deposició global és de 0.19 keq/ha/any. Aquests resultats indiquen que, a escala anual, les pluges de fang aporten suficient alcalinitat com per neutralitzar l'acidesa de la resta de les pluges. Les concentracions iòniques són elevades a les pluges de fang, i aquestes són per tant, un factor important en la deposició atmosfèrica de nutrients, encara que representen en promig només un 5.4% de la precipitació anual. Les pluges de fang són particularment riques en calci: la seva concentració mitjana ponderada d'aquest element és 14 vegades més gran que la de la resta de les pluges, i contribueixen amb un 46% a les entrades anuals de calci en la deposició global del Montseny.

## Introduction

Acid rain has been the subject of a vast research effort attempting to clarify the role of incoming atmospheric acidity in the alteration of biogeochemical cycles in terrestrial and aquatic ecosystems (Adriano & Havas 1989, Drablos & Tollan 1980, Hutchinson & Havas 1980, Reuss & Johnson 1986). Nevertheless, there are relatively few studies stressing the fact that particular areas frequently receive rain events of high pH (pH well above 5.6, the pH value of pure water equilibrated with atmospheric CO<sub>2</sub>).

Alkalinity responsible for this pH increase is mainly due to dissolution of alkaline components of aeolian soil dust. Khemani et al. (1987) found in India that highly alkaline pH values in cloud and rainwater were associated to high concentrations of dust particulates in the atmosphere. Buat-Ménard et al. (1974) reported observations of Ca<sup>2+</sup> enrichment in marine aerosols over the Atlantic which were attributed to soil dust from the Sahara and the Kalahari deserts. Löye-Pilot et al. (1986) observed in Corsica that rain with high concentrations of dust had an important Ca<sup>2+</sup> enrichment and high pH values. Dust collected in Corsica was traced back to originate in the Sahara desert. As a consequence, geographic areas in the vicinity of arid or denudated regions are subject to occasional episodes in which the atmosphere is loaded with Ca<sup>2+</sup>-Mg<sup>2+</sup> aerosols of high neutralizing capacity.

The Mediterranean is a particular example of such an area, being influenced by dust transport from North Africa, as has been widely reported (Bücher & Lucas 1984, Chester et al. 1984, Löye-Pilot et al. 1986, Martin-Vide & Moreno 1985). Bergametti et al. (1989) have identified several seasonal patterns of atmospheric circulation that produce transport of African dust over the Mediterranean. Saharan dust transport to southern Europe is revealed by the occasional occurrence of episodes of so-called red rain or red snow. At Barcelona, the average annual frequency of red rain events was 2.8 for the period 1944-1974, being concentrated mostly in spring and summer (Martin-Vide & Moreno 1985). Red rain episodes have been studied from a meteorological or mineralogical point of view (Bücher et al. 1983, Bücher & Lucas 1972, 1975, Clément et al. 1972), but the chemistry of red rains is poorly documented.

The purpose of this paper is to describe the chemistry of red-rains collected in a rural area of NE Spain and to evaluate their contribution to the annual input of nutrients and in the neutralization of acidic deposition. To that purpose we present data for a two-year period of weekly sampling of bulk precipitation in the Montseny mountains, distinguishing rain events containing red dust from events without red dust.

## Study area

The study site is located within the Estació Biològica de La Castanya

(41°46'N, 2°21'E) in the Montseny mountains, a predominantly forested massif which lies 25-30 km from the Mediterranean coast in northeast Spain. Agricultural land lie to the east and west of the mountain, its nearest industrial conurbation being that of Barcelona, 40 km to the SSW. The lithology of Montseny is mainly formed by low grade metamorphic schists and granodiorites.

The site of precipitation sampling is located in a forest clearing near the outlet of a small experimental watershed (TM9) which is routinely monitored for chemistry by our laboratory within the scope of a broader study of nutrient cycling in holm-oak (*Quercus ilex* L.) forests (Ávila 1988, Ávila & Rodà 1988, Ferrés et al. 1984, Rodà 1983, Rodà et al. 1990). The altitude at the site of precipitation sampling is 700 m a.s.l. Mean annual precipitation measured for 7 years at the site is 873 mm. Mean annual air temperature is estimated to be around 9°C. Vegetation of the watershed and on surrounding slopes is a dense, undisturbed forest of holm oak.

## Methods

Bulk precipitation for analysis was sampled with 4 collectors, each consisting of a polyethylene funnel 19 cm in diameter connected by a loop to a 10 L polyethylene bottle, following the Hubbard Brook design (Likens et al., 1977). Collectors are permanently open to the atmosphere, so the measured flux is bulk deposition which includes wet deposition and gravitatory sedimentation of particles. Weekly, rainwater samples (and occasionally snow collected by a 63-cm diameter bucket) were collected, and collectors were replaced by laboratory cleaned ones. The cleaning procedure consisted of a detergent wash of the disassembled parts of the collector, a rinse with abundant tap water followed by soaking in 10% diluted commercial HCl, and a rinse with abundant distilled water. Final conductivity of distilled water run through the assembled collector was checked to ensure that no contamination of HCl occurred. A plug of nylon mesh, also washed with distilled water and checked for conductivity, was placed in the funnel neck to prevent insects and large debris from reaching the collecting vessel. Infrequent samples with insects or debris were discarded. Usually, collectors were bulked by pairs to give two replicates for analysis, but for small rains (up to 5 mm) all collectors were bulked to give a single sample. Occasionally, the samples of the four collectors were analyzed. The amount of precipitation was measured by a standard rain-gauge at weekly intervals.

The day of collection, samples were taken to the laboratory, where pH and conductivity were measured after equilibrating the sample to the laboratory temperature. pH was measured potentiometrically using a combined electrode which was calibrated with pH buffers of 7 and 9, or 4 and 7 depending on the sample pH. Conductivity was measured after

calibration of the conductimeter with a 100  $\mu\text{S}/\text{cm}$  (at 20°C) solution. All red rains were filtered except for one (sample collected on 2 May 1985). Major ions were analyzed on frozen aliquots. Sodium and potassium were measured by atomic emission spectrometry, calcium and magnesium by atomic absorption spectrometry, and  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$  and  $\text{NH}_4^+$  by ion chromatography. Differences between collector replicates were nearly always less than 10%. In cases of higher differences, incoherent values could be easily identified and were discarded. Precision and accuracy were tested in all analytical runs and were found to be satisfactory (Avila 1988). Mean pH was calculated by transforming individual pH values to hydrogen concentration, weighting these by precipitation volume and reconvertng to pH.

We have no alkalinity data for the study period, so to obtain a tentative figure we have estimated the  $\text{HCO}_3^-$  concentrations from the equilibrium reactions of the carbonic acid-carbonate system:

$$\text{H}_2\text{CO}_3 = K_h \cdot p\text{CO}_2$$

$$\frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} = K_1$$

and merging the two equations,

$$[\text{HCO}_3^-] = k_h \cdot k_1 \cdot p\text{CO}_2 / [\text{H}^+]$$

Knowing the pH of individual rain samples,  $\text{HCO}_3^-$  can be found from the above relationship. We have taken an atmospheric  $p\text{CO}_2$  of 340 ppm as reflecting that of the rainwater samples, and values of  $k_h$  and  $k_1$  at laboratory temperature (20°C):  $k_h = 10^{-1.91}$  and  $k_1 = 10^{-6.38}$  (Drever 1982). From that we obtain:

$$[\text{HCO}_3^-] = 5.13 / [\text{H}^+] \text{ (concentrations in } \mu\text{eq L}^{-1}\text{)}$$

This relationship was applied to the  $\text{H}^+$  concentration for each sample, and  $\text{HCO}_3^-$  estimated values were thus obtained. These were then weighted by volume to obtain a  $\text{HCO}_3^-$  volume-weighted mean concentration.

## Results and discussion

Results reported here refer to the two-year period from 1 August 1983 to 31 July 1985. During this period 87 bulk precipitation weekly samples were collected, 8 of which were identified as red rains by visual observation of a coloured solid residue on funnel walls. Of the 8 red rains, 3 occurred in the first year (those collected on 16 April 1984, 6 May 1984 and 25 June 1984), and 5 in the second (collected on 12 November 1984, 25 April 1985, 2 May 1985, 21 June 1985 and 19 July 1985). The red rain on 19 July 1985 was very

small (0.1 mm) giving not enough volume for chemical analyses, and that of 16 April 1984 (1.3 mm) was discarded because of probable contamination; therefore, only the chemistry of the remaining 6 periods of red rain will be considered here (Table 1). As they were weekly samples, they may have included more than one individual red rain because red rains tend to be contiguous (Martin-Vide and Moreno 1985). The differences in precipitation chemistry found in this study between red and non-red rains are thus conservative estimates.

#### *Amount of precipitation*

The annual amount of precipitation at TM9 was 1052.5 mm and 873.0 mm for 1983-1984 and 1984-1985 respectively. The two year mean was 962.8 mm. The 8 weekly samples containing red rains delivered a total of 103.9 mm, or 52.0 mm yr<sup>-1</sup>. This amounts to 5.4% of the mean precipitation received at the site in this period. There was a nine fold difference in the amount of red

Table 1. Volume-weighted mean concentration in red rains and non-red rains for the two-year period 1983-1985 at Montseny. Conductivity in  $\mu\text{S cm}^{-1}$  at 20 °C; concentrations in  $\mu\text{eq L}^{-1}$ ; precipitation in mm yr<sup>-1</sup>.

Ion	Red rain	Non-red rain	Red/non-red rain
Conductivity	73.3	18.5	4.0
pH	7.76	4.68	—
H <sup>+</sup>	0.02	21.1	10 <sup>-3</sup>
Na <sup>+</sup>	98.6	21.6	4.6
K <sup>+</sup>	12.3	2.43	5.1
Ca <sup>2+</sup>	549	38.5	14.3
Mg <sup>2+</sup>	47.7	9.5	5.0
Mg <sup>+</sup>	26.7	4.6	5.8
NH <sub>4</sub> <sup>+</sup>	19.7	26.6	0.7
NO <sup>3</sup>	36.1	19.0	1.9
SO <sub>4</sub> <sup>2-</sup> *	140	50.5	2.8
SO <sub>4</sub> <sup>+</sup>	128	47.9	2.7
Cl <sup>-</sup>	126	26.0	4.8
HCO <sup>3-</sup> a	416	3.3	126
Precipitation	51.2 <sup>b</sup>	908 <sup>c</sup>	0.06
n	6	72	—

\* Mg<sup>2+</sup> and SO<sub>4</sub><sup>2-</sup> concentrations after correcting for sea-salt aerosol with Na<sup>+</sup> as reference ion.

<sup>a</sup> estimated from equilibrium reactions of the carbonate system, having considered a constant pCO<sub>2</sub> at 340 ppm and k<sub>1</sub> and k<sub>2</sub> values at 20 °C.

<sup>b</sup> non-analyzed and non-considered events totalled a further 1.4 mm yr<sup>-1</sup>.

<sup>c</sup> non-analyzed events totalled a further 3 mm yr<sup>-1</sup>.

rains between the two years: 10.6 mm in 1983-1984 vs. 93.3 mm in 1984-1985, accounting respectively for 1% and 10% of the annual precipitation. The greater amount of red rain recorded in the second year resulted from two large-volume events (50 mm collected on 12 November 1984 and 31 mm collected on 25 April 1985). These two storms account together for 88% of the total precipitation of red rains in the second year. Therefore, there is a high interannual variability in red rain amount of precipitation depending on the precipitation delivered by particular events. The amount of precipitation per period does not differ significantly between periods of red rain and periods of non-red rain (t test after logarithmic transformation,  $P > 0.05$ ).

### *Solutes in red rain*

The volume weighted mean concentrations of major ionic components in red rain and non-red rain samples collected at TM9 are given in Table 1. Except for  $\text{NH}_4^+$ , which is the sole ion to have similar concentrations in both type of rains, and for  $\text{H}^+$  which decreases in red rains, all ions have much greater concentrations in red rains. Differences are significant for all ions ( $P < 0.005$  for conductivity, pH,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{SO}_4^{2-}$  and  $\text{Cl}^-$ ;  $P = 0.09$  for  $\text{NO}_3^-$ ) except for  $\text{NH}_4^+$  ( $P = 0.22$ ) when applying a covariance analysis with amount of precipitation as a covariate. Sodium,  $\text{K}^+$ ,  $\text{Mg}^{2+}$  and  $\text{Cl}^-$  means in red rains are greater by a factor of 4 or 5 than non-red rains, while for  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  this factor is 2 and 3 respectively (Table 1). However, the ion with the highest difference is  $\text{Ca}^{2+}$ , whose mean concentration in red rains is 14 times that of non-red rains. The above mentioned higher ion concentrations are reflected in conductivity, which consequently is greater in red rains. As stated before,  $\text{H}^+$  concentration is very low in red rains, giving a volume-weighted mean pH of 7.76. This value contrasts strongly with the mean pH of non-red rains of 4.68 (Table 1). The temporal variation of pH in bulk deposition at TM9 is presented in Figure 1, red rains differing from non-red rains because of their higher pH values. Red rains are characteristically very concentrated in all ions, but they show also a high variability in concentrations, with coefficients of variation (%) of 35.2 for conductivity, 56.0 for  $\text{Na}^+$ , 56.1 for  $\text{K}^+$ , 42.9 for  $\text{Ca}^{2+}$ , 25.8 for  $\text{Mg}^{2+}$ , 68.1 for  $\text{NH}_4^+$ , 49.7 for  $\text{NO}_3^-$ , 55.8 for  $\text{SO}_4^{2-}$  and 54.0 for  $\text{Cl}^-$ , for the 6 red rain events at TM9.

Red rains could be distinctly differentiated from non-red rains by means of a principal component analysis applied to the matrix of the 9 analyzed variables (pH,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{NH}_4^+$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$  and  $\text{Cl}^-$ ) and 85 valid weekly samples. The graphical expression of the analysis is shown in Figure 2, where the three first components account for 91.7% of rainwater ionic variation. Red-rain samples form a distinct group when individual scores are represented for the first component (identified as mineralization or richness in  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$ ,  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$ ) and the third component (defined by pH

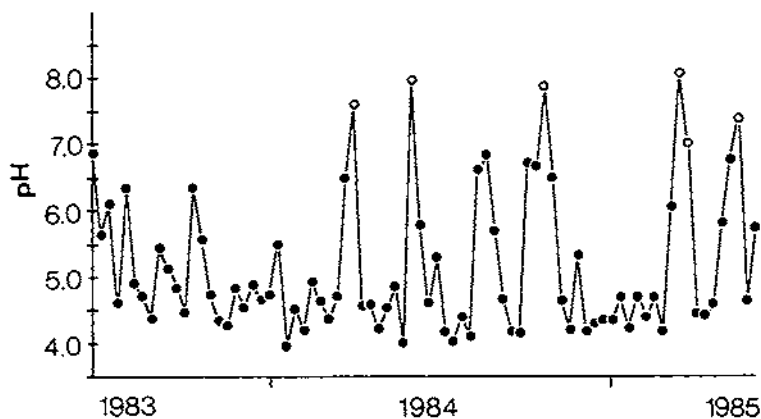


Figure 1. Temporal variation of bulk precipitation pH at TM9. Red rains are represented by open circles.

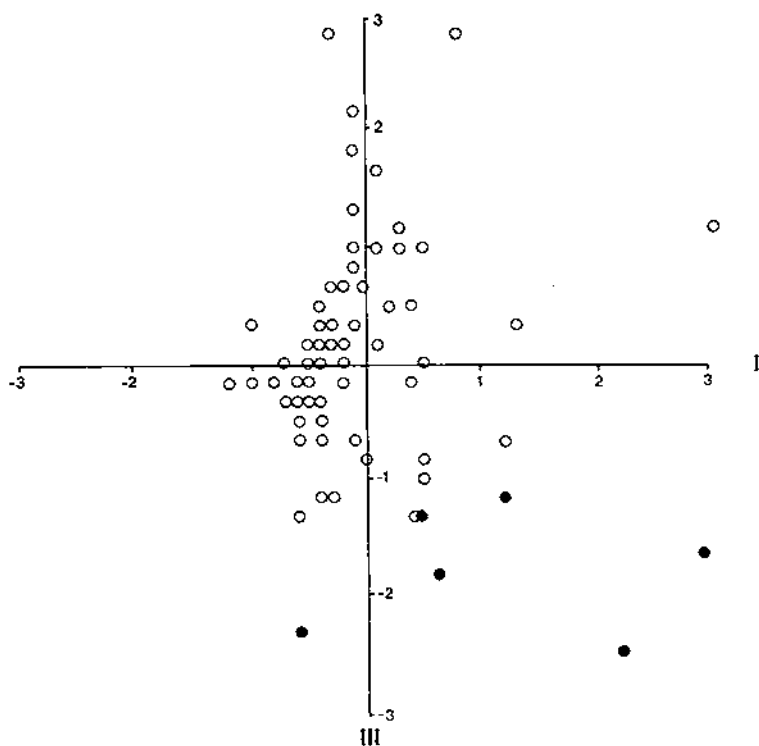


Figure 2. Results of principal component analysis of bulk precipitation chemistry for all the weekly samples, defined by their pH and major ion concentrations. Scores for individual rain samples defined by the first and third components. Red rains are represented by filled circles.

and  $\text{NH}_4$  and identified as acidity-alkalinity of rain). Red rains are differentiated from the rest of rains because of their high mineralization and high pH values (Fig. 2) as is reflected by results in Table 1. At this moment, it is worth stressing that red-rains were defined by usual recognition of coloured marks of deposited dust. It is possible that, because of the weekly sampling schedule, some red rains falling at the beginning of the period and followed by non-red rains were missclassified, or conversely, red rains at the end of the period could contain non-red rains collected at the beginning of the period. In both cases, the mixing would produce a dilution of the usual high concentrations of red rains, and probably, a decrease in the sample pH. These samples, and others influenced by dust aerosols but not leaving visual marks, would fall in the vicinity of the red rain group in the principal component analysis, and they might be as well some of the points of relatively high pH in Figure 1 which are not signaled as red rains.

Not only do red rains differ widely from non-red rains in their ionic concentrations, but also their relative ionic proportions are quite distinct. Particularly interesting is the ratio of non-sea salt  $\text{Ca}^{2+}$  to non-sea salt  $\text{Mg}^{2+}$  (also called excess Ca and excess Mg and represented by  $\text{Ca}^*$  and  $\text{Mg}^*$ ). In fact, as only 2% of  $\text{Ca}^{2+}$  in bulk precipitation at Montseny comes from sea salt aerosols, we have computed excess  $\text{Ca}^{2+}$  only for consistency with  $\text{Mg}^{2+}$ . At Montseny, non-red rains have a remarkably constant  $\text{Ca}^*/\text{Mg}^*$  ratio of about 8, on an equivalent basis. This gives a high linear correlation between  $\text{Ca}^*$  and  $\text{Mg}^*$  (Fig. 3). This constancy of the  $\text{Ca}^*/\text{Mg}^*$  ratio implies that either (i) all major continental sources of soluble  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  in non-red rains at Montseny yield a  $\text{Ca}^*/\text{Mg}^*$  ratio of about 8, or (ii) different sources with varying proportions of soluble  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  always combine in such a manner to give the observed  $\text{Ca}^*/\text{Mg}^*$  ratio. In contrast, red rains are clearly set apart from non-red rains in a scattergram of  $\text{Ca}^*$  versus  $\text{Mg}^*$  (Fig. 3). In proportion to  $\text{Mg}^*$ , red rains are much richer in  $\text{Ca}^{2+}$  than non-red rains, their  $\text{Ca}^*/\text{Mg}^*$  ratio between volume-weighted means rising to 21 on an equivalent basis. This sharp difference in ionic proportions provides further evidence that the source areas of air-borne matter are different for red and non-red rains.

Two other studies of bulk deposition in Catalonia have distinguished between red and non red rain events. One was carried at a nearby station named TM5 which is located in culminal heathlands in the Montseny and is only 1.35 km away from TM9. The other one was carried at Prades (Tarragona), 120 km to the WSW from our study site. At TM5, ten red rains were identified by visual observation of reddish marks on collectors between January 1982 and December 1984. Of these, only the arithmetic mean concentration is available (Belillas 1989) which is given in Table 2. For comparison, the arithmetic mean concentration of the 6 red rain events collected at TM9 is given in Table 2. Red rains in both stations show similar features in: 1) basic pH and 2) very high ionic concentrations, particularly



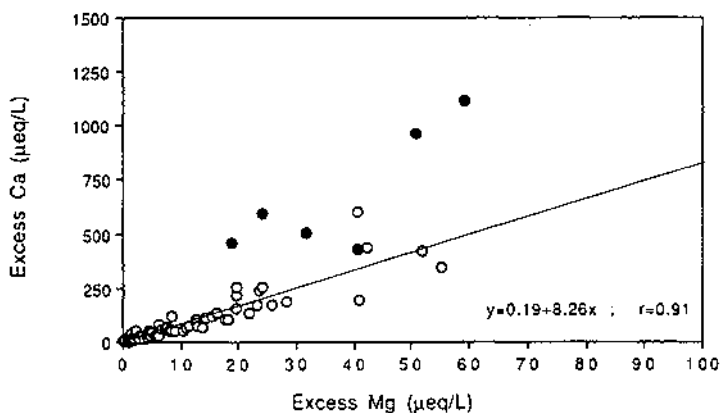


Figure 3. Scattergram of non-sea salt ('excess') Ca concentration versus non-sea salt Mg concentration in bulk deposition at TM9. Red rains are represented by filled circles. Points not marked as red rains but which are well above the regression line could be red rains not identified as such in the field. Regression has been computed only with non-red rains.

Table 2. Arithmetic mean chemistry of red rains in three localities of northeastern Spain. Concentrations in  $\mu\text{eq L}^{-1}$ . Conductivity in  $\mu\text{S cm}^{-1}$  at 20 °C. Precipitation in mm.

Variable	Montseny		Prades <sup>c</sup>
	TM9 <sup>a</sup>	TM5 <sup>b</sup>	Bosc Poblet
pH	7.66	6.24	7.07
Na <sup>+</sup>	75.3	148	57.7
K <sup>+</sup>	16.6	26.1	8.9
Ca <sup>2+</sup>	708	750	199
Mg <sup>2+</sup>	53.1	91.2	20.7
NH <sub>4</sub> <sup>+</sup>	25.3	62.7	24.9
NO <sub>3</sub> <sup>-</sup>	52.2	110	22.6
SO <sub>4</sub> <sup>2-</sup>	211	317	67.2
Cl <sup>-</sup>	97.1	178	53.3
HCO <sub>3</sub> <sup>-</sup>	—	291 <sup>d</sup>	201
Precipitation	102.3	281	312
n	6	10	6

<sup>a</sup> This study. August 1983 to July 1985.

<sup>b</sup> Belillas 1989. January 1982 to December 1984.

<sup>c</sup> Piñol 1990. September 1986 to June 1988.

<sup>d</sup> Mean of 5 samples.

for  $\text{Ca}^{2+}$ . At TM5, averaged red rain concentrations are even higher than at TM9. Because of the observed variability in red rain chemistry, it is possible that events collected at TM5 before the onset of the TM9 monitoring period were very concentrated producing the observed differences in Table 3. When comparing red to non red rains at TM5 (in terms of arithmetic mean concentrations), red rains were higher than non red rains by a factor of 8 for  $\text{Ca}^{2+}$ , by a factor of 4-5 for  $\text{Cl}^-$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$  and  $\text{Na}^+$ , and by a factor of 2-3 for  $\text{NH}_4^+$ ,  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  (Belillas 1989), results similar to those obtained at TM9, except for  $\text{NH}_4^+$ .

At Prades, red rains were identified by the same procedure, and for the period September 1986 to June 1988, 6 red rain events were obtained (Piñol 1990). Their arithmetic mean concentration is given in Table 2. Red rains at Prades are similar to those of Montseny in that they present a basic pH, but they differ in that they are appreciably more diluted. However, when red rains are compared to non red rains, they are higher by a factor of 4 for  $\text{Ca}^{2+}$ , and of 2 for  $\text{Na}^+$ ,  $\text{Mg}^{2+}$  and  $\text{Cl}^-$ . Weak differences for  $\text{K}^+$ ,  $\text{NH}_4^+$ ,  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  exist (Piñol 1990). Differences in the sampling period and geographical location could account for distinct chemistry of red rains between Prades and Montseny (in fact, recent red rains collected at TM9 are also more diluted).

From the above studies it is clear that red rains are typically enriched in  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Cl}^-$  and  $\text{Na}^+$ , and have high pH values. According to this basic pH, alkalinity measured at TM5 and at Bosc de Poblet give high values (Table 2).

### *Origin of ions*

High  $\text{Na}^+$  and  $\text{Cl}^-$  concentrations in rainwater are due to sea salt aerosol enrichment of air masses in contact with sea surfaces (Eriksson 1952, Junge & Werby 1958). Air masses producing red rain over the Montseny mountains may have to travel over long distances on the Mediterranean sea, thus having the opportunity of a sea salt aerosol enrichment, but this can hardly account for the 5 fold enrichment in  $\text{Na}^+$  and  $\text{Cl}^-$  of red rains respect to non red rains. Probably, soil dust from aridic regions contained in red rains also contributes to enrich rain with  $\text{Na}^+$  and  $\text{Cl}^-$ .

Sea salt aerosols also would provide other ions, particularly  $\text{Mg}^{2+}$  and  $\text{SO}_4^{2-}$ . For these two ions, however, differences between red rains and non red rains persist after correcting for the sea salt contribution (Table 1). The method of correction is given in the footnotes of the table. Excess  $\text{Mg}^{2+}$  concentration in red rains may come from solubilization of dolomite present in dust particles. As it has been found in 9 analyses of particulate matter of red rain over Barcelona, dolomite is present in percentages between 1 to 4 % (R. Julià, unpublished. data). Excess  $\text{SO}_4^{2-}$  in red rains may be supplied through one or more of these mechanisms:

- a) solubilization of gypsum minerals contained in red dust,
- b) solubilization of sulphate salts accumulated in arid soils which are not detected as gypsum and are incorporated to red dust,
- c) incorporation of oxidated biogenic S emitted over the Mediterranean sea to air masses which produce red rain, and
- d) incorporation of  $\text{SO}_2$  and other  $\text{SO}_4^{2-}$  precursors from industrial emissions to red rain air masses.

Of these factors, the first may be of little importance: it has been found that only 2 out of 9 analysed samples of red dust over Barcelona contained gypsum, and moreover, their content was very low (0.4-0.8%, R. Julià, unpublished data). Löye-Pilot et al. (1986) reported some gypsum in Saharan dust samples collected in Corsica in concentrations lower than 2%. Referring to point d) above, red rain trajectories usually pass over scarcely industrialized areas of north Africa and south Spain, and over the Mediterranean sea, so anthropogenic emissions rarely can account for the observed  $\text{SO}_4$  excess in red rains, though the Barcelona conurbation could have some effect. In reference to point e) little information is available of Mediterranean biogenic sulphur emissions, although they seem to be important in open oceans (Bates et al. 1987, Charlson et al. 1987). Even if biogenic emissions were important, there is no reason to think they differentially enrich red rain air masses. We can consider the possibility that edaphic particles containing non-gypsum sulphate salts accumulated by evaporation in aridic soils (point b) could be a source of excess  $\text{SO}_4^{2-}$  in red rains over northeastern Spain. At present we have no data to support this.

#### *Red rains as a neutralizing agent*

At TM9, TM5 and Bosc de Poblet, the parameters that show the highest difference between red and non-red rains are  $\text{Ca}^{2+}$  and pH, as it has been found also by other authors (Löye-Pilot et al. 1986). The high content of  $\text{Ca}^{2+}$  in red rains and its direct relationship to pH has to be related to the solubilization of calcite, which in red rain dust has been found to range between 5 to 30%, with more frequent values of 20 to 30% (Bücher & Lucas 1975, 1984, Bücher et al. 1983, Clément et al. 1972, Löye-Pilot et al. 1986). In 9 samples of red dust over Barcelona, calcite content was between 7 and 18% (R. Julià, unpublished data). The dissolution of calcite in rainwater would provide  $\text{Ca}^{2+}$  and  $\text{CO}_4^{2-}$  ions. Carbonate ions would combine with  $\text{H}^+$  to give the observed high pH values in red rain (Fig. 1) and to produce  $\text{HCO}_3^-$  ions. We have not a complete data set of bicarbonate alkalinity in red rains for the 1983-1985 period but we have indication that it must be high because at TM5, only 1.35 km away from our station, the arithmetic mean alkalinity for 5 red rain events between 1982 and 1984 was 291  $\mu\text{eq/L}$  (Belillas 1989, Table 2). More recent measurements (1984-1988) at our site give a volume weighted mean alkalinity of 193  $\mu\text{eq/L}$  for 10 red rain events. The mean

$\text{HCO}_3^-$  concentration during the study period in this paper, estimated from the equilibrium reactions of the carbonic acid-carbonate system, produces a weighted mean concentration in red rains of  $416 \mu\text{eq/L}$ , while in non-red rains it is of  $3.3 \mu\text{eq/L}$ . If we calculate the overall value for all rain events during the two-year period, the estimated  $\text{HCO}_3^-$  volume weighted mean concentration of bulk deposition is  $25.3 \mu\text{eq/L}$ . Deduced from these estimated values,  $\text{HCO}_3^-$  input in red rains accounts for 88% of the annual  $\text{HCO}_3^-$  input.

#### *Nutrient input in red rains*

Nutrient input values depend on nutrient concentrations in rainwater, and on precipitation amounts. Red rains have very high nutrient concentrations as compared to non-red rains (Table 1), so, although they deliver only 5.4% of the annual precipitation for the study period, they contribute to annual inputs with quite important amounts (Table 3). This is particularly true for  $\text{Ca}^{2+}$ : red rains are responsible for nearly half the  $\text{Ca}^{2+}$  input in bulk precipitation for the two-year period. For  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$  and  $\text{Cl}^-$ , red rain contribution to annual inputs is about 20%, while for  $\text{NO}_3\text{-N}$  and  $\text{SO}_4\text{-S}$  it is about 10% (Table 3).

These percentages may vary sharply from year to year, depending mainly on red rain precipitation amount. For example, red rain  $\text{Ca}^{2+}$  input in 1983-1984 was 24% of annual input, while in 1984-1985 it was 52%. In the second year, there were two single red rain events of abundant precipitation (12 November 1984 and 25 April 1985) and high  $\text{Ca}^{2+}$  concentration which delivered  $4.8 \text{ kg Ca}^{2+} \text{ ha}^{-1}$  and  $3.2 \text{ kg Ca}^{2+} \text{ ha}^{-1}$  respectively, which accounted for 27% and 18% of the annual  $\text{Ca}^{2+}$  inputs. Hence, years with abundant red rain will have greater  $\text{Ca}^{2+}$  inputs as compared with years of little red

Table 3. Annual bulk deposition inputs in red rains compared with non-red rains at Montseny for the period 1 August 1983 to 31 July 1985. In  $\text{kg ha}^{-1}\text{yr}^{-1}$ .

Element	Red rain input	Non-red rain input	Annual input	% due to red rain
$\text{H}^+$	$1.09 \cdot 10^{-5}$	0.19	0.19	$5.5 \cdot 10^{-5}$
$\text{Na}^+$	1.16	4.51	5.67	20.5
$\text{K}^+$	0.25	0.86	1.11	22.3
$\text{Ca}^{2+}$	5.63	7.00	12.6	44.5
$\text{Mg}^{2+}$	0.30	1.05	1.35	22.0
$\text{NH}_4\text{-N}$	0.14	3.39	3.53	4.0
$\text{NO}_3\text{-N}$	0.26	2.42	2.68	9.6
$\text{SO}_4\text{-S}$	1.14	7.35	8.49	13.4
$\text{Cl}^-$	2.29	8.38	10.7	21.5

rain, and thus, red rain episodes confer great interannual variability and difficulty in the establishment of time trends for the inputs of  $\text{Ca}^{2+}$  (and other ions). This is important when studying input and output budgets for watersheds because net outputs (outputs minus inputs) will vary depending on the magnitude of red rains.

Finally, from the estimated alkalinity values in bulk deposition for 1983-1985, an annual dissolved  $\text{HCO}_3^-$  input of  $0.24 \text{ keq ha}^{-1} \text{ yr}^{-1}$  is a result. For the same period, the hydrogen input in bulk deposition is  $0.19 \text{ keq ha}^{-1} \text{ yr}^{-1}$ . These results indicate that, on an annual basis, acidity due to non-red rain episodes has been neutralized, red rains contributing 88% to the neutralizing capacity. Moreover, particulate matter coming in red rains has also a neutralizing capacity due to its calcite content. If we take a value of 12%  $\text{CaCO}_3$  content in particulate matter (mean of 7 analyses of red rain dust collected in Barcelona, R.Julià com. pers.) and we consider the particulate input of the  $19.0 \text{ g/m}^2$  in the 2 rainiest events in the period (which is a minimum estimate), calcite would add  $0.24 \text{ keq ha}^{-1} \text{ yr}^{-1}$  alkalinity thus providing an even more alkaline budget to the ecosystem. It seems that Mediterranean ecosystems in the reach of Sahara air masses have alkaline inputs great enough to neutralize acidic inputs. We expect to corroborate that statement with the alkalinity measurements now routinely undertaken.

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