

Rainwater in the Massif Central (France); a global geochemical approach: major and trace elements, and isotopic (Sr, Pb) constraints

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Aerosols are the main source of chemical elements carried by rainwater. The atmosphere, by means of either aerosols or rainwaters, has been recognized as an important source of chemical species in soils and rivers. The dissolved components in rainwater are derived from sea salt aerosols, from terrestrial aerosols (soil dust, biological emissions) and from anthropogenic sources (industry, agriculture, burning of vegetation and fossil fuels, fertilizers). Terrestrial aerosols may originate from soil erosion near the collector (local source), from distant areas within the continent (external source), or even from other continents (exogenic source). Likewise, aerosols derived from anthropogenic sources may originate in the vicinity of the collector (local source) or far from it (distant source).

One aim of this study was to use strontium isotope ratios correlatively with major and trace elements in order to determine the different sources (sea salt and crustal sources) of chemical elements in rainwaters [1]. The proportions of the various inputs (marine, distant or local) are determined in this study. A second aim was to look at the behaviour of trace metals in rainwaters in terms of wet deposition and source regions of dusts in the centre of France with constraints added by the measurement of lead isotopes [2].

Collection procedure and sampling site

An automatic precipitation sampler was designed and constructed at BRGM for collecting rain for chemical and isotope analyses. Each sample represents a monthly series of rain events [1]. The basic requirements for our collector were automatic detection and collection of rainfall, elimination of dry fallout, collection of frozen precipitation, and avoidance of sample contamination for the elements studied. The sampling site is in an open area (altitude 340 m), far from dirt roads or other sources of contamination, in the Massif Central (France)

between Issoire and Clermont-Ferrand, and was selected to minimize local sources of contamination. The strontium and lead isotope ratios, and major- and trace-element concentrations were measured in rainwater samples collected over a period of 15 months.

Chemical and isotopic data

Concentrations of several elements varied greatly during the sampling period. Five ions were clearly predominant. Ca and Na were the most abundant cations with a mean weighted concentration of 17.7 and 14 $\mu\text{mole/L}$, respectively. Mg was the least abundant of the major cations with a mean weighted content of 2.8 $\mu\text{mole/L}$. No anion was strongly dominant. The mean weighted contents of Cl (19 $\mu\text{mole/L}$), SO_4 (23 $\mu\text{mole/L}$) and NO_3 (26 $\mu\text{mole/L}$) were similar.

Trace-element concentrations in the rainwater samples varied greatly. The highest variation occurs for lead (factor greater than 500) the lowest for Sb (factor of 14); Cd has a factor close to 60; and Zn and Cu have a factor close to 30. For Ni, which is not systematically detected, the fluctuation in Sr ranged between 0.004 $\mu\text{mole/L}$ and 0.034 $\mu\text{mole/L}$.

The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of rainwaters collected over the Massif Central ranged between 0.709198 and 0.713143. The lead isotopic compositions range from 17.935 to 19.22 for $^{206}\text{Pb}/^{204}\text{Pb}$; from 15.578 to 15.73 for $^{207}\text{Pb}/^{204}\text{Pb}$ and from 37.559 to 38.606 for $^{208}\text{Pb}/^{204}\text{Pb}$.

Discussion

Using Na as an indicator of marine origin, and Al for the crustal input in rain samples, the proportion of marine and crustal elements was estimated from elemental ratios. We determined a marine origin of 4 to 100% for Cl, of 0.6 to 20% for SO_4 , of <1 to 10% for Ca, <1 to 40% for K, 4 to 100% for Mg and 1 to 44% for Sr.

Strontium isotopes were used to characterize the crustal sources. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the crustal sources varied considerably from 0.7092 to 0.71625 and indicate the occurrence of multiple sources for the crustal component in the analysed rainwaters [1]. One of the terrestrial components can be related to calcic particles from soil or limestone dusts. This input of carbonate particles to the atmosphere could originate near the sampling site or from a more remote source (i.e. carbonaceous deposits from the Paris and Aquitaine basins). The second end member was related to dust emissions from silicate from the Massif Central and from other granitic areas bordering the Massif Central (Margeride, Morvan, Lozere). The last end member is made up of anthropogenic input such as fertilizers.

The variations in trace-metal concentrations can be mostly related to variations in the aerosol sources like the relative proportions of trace-metal-bearing phases and anthropogenic sources (industry, agriculture, burning of vegetation and fossil fuels, fertilizers). None of the trace-element contents exhibit correlation with the rainfall amount and no inter-element relationships can be viewed in the database. The high contents induce a high wet deposition rate, clearly higher than that found in unpolluted areas. Lead

(mean value $996 \mu\text{g}/\text{m}^2$ /year) is the most carried trace metal in these rains, and the antimony element (mean annual value is $1.12 \mu\text{g}/\text{m}^2$ /year) is the least carried.

A five component mixing model can be supposed to explain the scattering of data in the classical isotope correlation ($^{206}\text{Pb}/^{204}\text{Pb}$ vs $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{206}\text{Pb}/^{204}\text{Pb}$ vs. $^{208}\text{Pb}/^{204}\text{Pb}$). The five different signatures consist of (i) a gasoline component, (ii) a natural background component approached through pre-industrial sediments, (iii) industrial inputs, for which the multiplicity of sources induces difficulties in constraining this end-member, (iv) an agricultural signature from amendments, and (v) a carbonaceous source – a signature from residues of mining activities. However, it is not possible to calculate the respective contribution of each end-member because they all plot on a straight line.

References

- [1] Negrel, Ph. and Roy S. (1998) *Appl. Geochem.*, in press.
- [2] Cocherie, A., Negrel, Ph., Roy, S. and Guerrot, C. (1998) *J. Analytical Spectrometry*, in press.