Rainfall chemistry in the south of France (Hérault, 1996–1997)

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A global study by BRGM on groundwater hydrosystems, helps better understanding of groundwater processes in karstic areas of Southern France. A chemical and isotopic characterisation of input signal has to be carried out in order to assess the origin of dissolved constituents measured in precipitation and to evaluate the relative contribution of natural and antropogenic emissions. For this purpose, rainfall in the south of France (Herault) was collected during the hydrological cycle 1996-1997 and analysed for major ions and water stable isotopes.

Geological setting

The location of rainfall gauges are presented in Fig. 1. The sampling network includes 4 rainfall gauges installed along an altudinal transect (Mireval: 6 m ; St-André: 71 m; Guzargues 125 m and Rogues 573 m). Two distinct geological areas can be distinguished (1) limestone plateau to the North (Guzargues and Rogues) and the alluvail plain of the Hérault river to the South (St-André and Mireval).

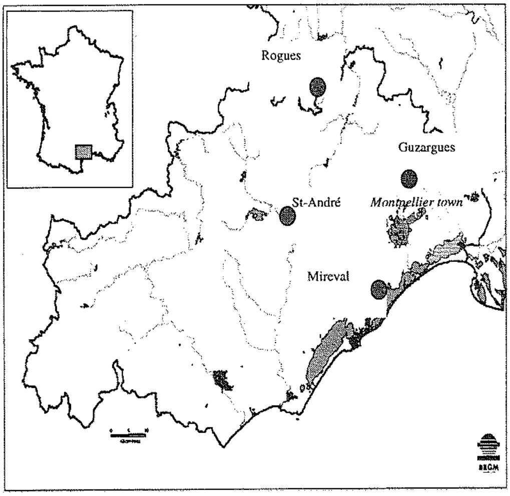

FIG. 1. Localization of sampling site.

Analytical methods

Samples were collected after rainfall events in polyethylene bottles and filtered using a 0.45 µm Millipore filter. Major element analyses were carried out with ionic chromatography for the anions, and with ICP-MS for cations. ^{18}O and ^{2}H isotopic analyses were performed with a mass spectrometer at the BRGM laboratories.

Results

The mean weighted concentration for bulk precipitation (wet plus dry) collected in the 4 stations is shown in Fig. 2.

The largest ionic concentration is detected at the Mireval station which is close to the sea (6 km). The ionic contents of other stations discreases according to both distance from the sea and elevation.

For each station, the regression line between Na and Cl concentrations is reported in Table 1. The ratio of Na to Cl of each station is similar to the commonly used ratios in bulk seawater 0.55 (Berner and Berner, 1987). Consequently, Cl can be considered as a conservative tracer and used to

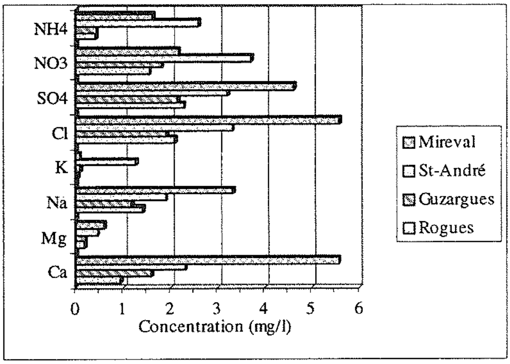

FIG. 2. Weighted mean concentration of major ions in bulk precipitation during Oct- 1996-Sept-1997 period.

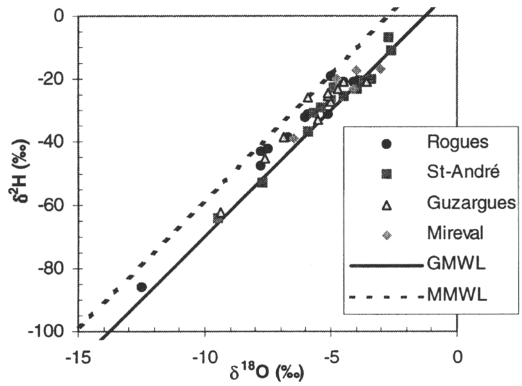

FIG. 3. Relationship between $\delta^{18}O$ and δ^2H in precipitation. GMWL and MMWL represent the Global Meteoric Water Line: $\delta^2H = 8\cdot\delta^{18}O + 10$ and the Mediterranean Meteoric Water Line: $\delta^2H = 8\cdot\delta^{18}O + 22$, respectively.

TABLE 1. Parameters of Na-Cl correlation lines calculated for all samples of each station

Name station	Slope	Intercep	r coefficient
Rogues	0.45 (± 0.53)	0.04 (± 0.10)	0.963
Guzargues	0.49 (± 0.35)	0.03 (± 0.11)	0.957
St André	0.52 (± 0.25)	0.01 (± 0.08)	0.998
Mireval	0.58 (± 0.21)	0.07 (± 0.51)	0.935

estimate sea contribution for other ions. The sea-salt contribution can be estimated by:

$$f(Xi) = (Xi/Cl)ss*(Cl/Xi)r$$

where Xi is the concentration of the investigated element, the subscript "ss" and "r" designate sea-salt and rainwater assuming that all the Cl anion is exclusively of marine origin and that the ratio Xi/Cl is preserved during transport from sea surface to atmosphere.

The mean-marine contributions of major ions calculated for 96-97 hydrological cycle are given in Table 2. The Mg rain concentration of the Rogues, Guzargues and Mireval stations is strongly influenced by sea-salt origin (60%). For the St-André station, the influence of sea-salt to the Mg budget is lower (about 30%). Concerning other major ions, the contribution of sea-salt is lower.

TABLE 2. Mean marine contribution to observed concentrations of major ions in rainwater for the 1996-1997 hydrological cycle (all figures %)

Name station		Mg	K	Ca	SO_4	NO_3
Rogues						
	Mean	63	14	4	11	7
	S. D.	*21*	*13*	*2*	*8*	*4*
Guzargues						
	Mean	56	7	3	14	8
	S. D.	*28*	*5*	*3*	*12*	*9*
St-André						
	Mean	32	3	2	10	8
	S. D.	*23*	*3*	*4*	*11*	*12*
Mireval						
	Mean	62	12	4	19	22
	S. D.	*39*	*17*	*6*	*15*	*25*

S. D. = Standard deviation

The enrichment relative to sea-salts is due to the contribution of non marine source. In the Mediterranean area, the Ca excess found in rainwater can originate from soil particles, mainly limestone. The SO_4 and NO_3 excess can be related to the influence of human activity (SO_2 emission by factories and NOx emission by traffic). The SO_4 excess in rainfall is however greater than NO_3 excess, except for the St-André station. This result does not mean necessarily that industrial pollution is greater than traffic pollution. Indeed, the high correlation between Ca and SO_4 suggests that a large part of Ca and SO4 found in precipitation is due to the dissolution of gypsum particles originating from Saharan dust (Loÿe-Pillot *et al.*, 1986).

In $\delta^{18}O$-δ^2H diagram (Fig. 3), samples are distributed between the Global and Mediterranean Meteoric Water Lines, each characterised by different deuterium excess (10 and 22‰ respectively, Dansgaard (1964), Rozanski *et al.*, 1993).

Deuterium excess values ranged from 7.2 to 21.4‰ (arithmetic mean = 13.6 ± 0.5‰) without any clear seasonal trend. This suggests that summer and rainfalls were generated with both air masses from Atlantic and Mediterranean sea.

References

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