

Occurrence of mineral water springs in the stream channel of the Allier River (Massif Central, France): chemical and Sr isotope constraints

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Abstract

The French Massif Central has long been recognized as an area with numerous mineral water springs. It is often very difficult to measure the flow rate of mineral springs since they are spread out over extensive areas. Water from the Allier River has been sampled monthly over a 13-month period and a spatial cross-section survey carried out at base flow conditions in order to estimate the discharge of mineral water in the Allier River streambed.

For the monthly survey, the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios vary between 0.709511 and 0.712656. A good correlation exists between $^{87}\text{Sr}/^{86}\text{Sr}$ and $1/\text{Sr}$ ratios and defines binary mixing between mineral waters and the Allier River *sensu-stricto*. The mixing processes have been studied using the Sr isotopic systematic and a conservative species (chloride). Except for one sample, the mineral water input never exceeds 2%. However, the mineral water discharge into the Allier streambed could not be precisely estimated because effluent seepage of mineral water may occur in a part of the channel representing only a small volume of the cross-sections.

Variations in the solute concentrations across the river channel were measured at 14 sites chosen as being representative of areas where: (a) mineral water emerges, (b) no mineral water emerges, and (c) mixing is complete. A model developed for the monthly study using Cl as a reference was used in the spatial survey. The input of mineral water in the Allier streambed ranges from 0.1–0.15% in most of the samples and is greater than 2% at two points. The general mass balance of the proportions of mineral water and Allier River water (*sensu-stricto*) using the sum of cations and anions was calculated and the input of mineral water into the Allier streambed was determined at the cross-section nearest the Allier gauging station (0.134%). The discharge of the Allier River at the gauging station was about $17.7 \text{ m}^3/\text{s}$ during the sampling period, which gives a discharge of mineral water of about $0.02 \text{ m}^3/\text{s}$ into the Allier channel. © 1997 Elsevier Science B.V.

Keywords: Massif Central; France; Dissolved load; Allier river; Mineral waters; Strontium isotopes

1. Introduction

The French Massif Central has long been recognized as an area with numerous mineral water springs (Michard et al., 1976; Fouillac, 1983), many of which are used for health cures or for bottled mineral water.

Major studies have been carried out since 1976 by BRGM (Bureau de Recherches Géologiques et Minières) and others on gases (Batard et al., 1982) and on the chemistry of thermo-mineral waters (Fouillac et al., 1975; Fouillac, 1983; Sanjuan et al., 1988; Négrel et al., 1997a). However, it remains difficult to measure the total discharge of springs, which is needed to estimate the size of the mineral water resource.

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The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of mineral waters have been used to provide information on mixing processes (Michard et al., 1976; Stetler, 1977; Stetler and Allegre, 1978) and recently, a small watershed in the Cézallier area has been studied in order to determine the area of effluent mineral water seepage and quantify mineral water input to the river (Négrel et al., 1997b).

The aim of the present study is to evaluate the discharge of mineral water in the Limagne d'Allier, more precisely in the Allier River streambed. The Limagne d'Allier is a flood plain of the Allier River (Fig. 1a and 1b) with numerous mineral springs in the area. Seepage of mineral water is also clearly visible in the Allier streambed through CO_2 bubbles in the water mass. A chemical and isotopic survey has been carried out over one year to characterize and estimate the mineral water input into the river. Major elements (Ca, Na, Mg, K, Cl, SO_4), one trace element (Sr) and strontium isotope ratios ($^{87}\text{Sr}/^{86}\text{Sr}$) were measured in monthly samples of Allier River water. During base flow conditions in August 1995, a cross-section sampling survey of the Allier River channel was then carried out along a 29-km stretch of the river, and major elements were measured (Ca, Na, Mg, K, Cl, SO_4) in order to determine the discharge of mineral water input into the streambed.

2. Sampling procedure and analytical methods

2.1. The monthly and spatial survey of the allier river; mineral water investigation

Allier River water was sampled every month near Sainte Marguerite (Fig. 1b), with a total of fifteen samples taken over the 13-month study period (February 1994–April 1995) at the same location, regardless of the river discharge. The discharge near the sampling point was obtained from the French Department of Public Works. The spatial survey was carried out during base flow conditions in August 1995 along a 29-km stretch of the river. Several channel cross-sections were studied and 2 to 6 points were sampled between the two banks at 14 different locations (Fig. 1b); samples were analysed on site for major elements.

Water from all of the mineral springs in the area was sampled and analysed for major and trace elements and Sr isotope ratios. The chemical and isotopic characteristics of the mineral water end-member were determined and the detailed results have been presented in a companion paper (Négrel et al., 1997a); the results are summarized in Table 1.

2.2. Analytical methods

River water samples were filtered on site through $0.2\ \mu\text{m}$ acetate cellulose filters and stored in pre-cleaned polypropylene bottles, acidified to pH 2 with ultrapure HNO_3 , and used for cation and isotope measurements. One bottle was not acidified and was used for anion determination.

Electrical conductivity and water temperature were measured using a WTW LF96 microprocessor conductivity meter standardized to $20\ ^\circ\text{C}$. The pH was measured on site using an Ingold combined pH electrode and an Orion 250 pH-meter previously calibrated using two standard buffers. Chemical analysis of water samples was carried out by capillary ion electrophoresis for major cation and anions (Pantsar-Kallio and Manninen, 1995) and atomic absorption spectrometry for Sr. Precision was greater than $\pm 5\%$ for the determination of major elements and 10% for Sr measurements.

The standard procedure used by BRGM was adopted for chemical separation and mass spectrometry for strontium. Briefly, Sr was separated using a cation exchange column (DOWEX AG50X8) with $\text{HCl}\ 2\text{N}$ as eluant. The total blank for Sr was less than $0.5\ \text{ng}$ for the entire procedure (sampling, filtration, storage and chemical separation). After chemical separation, $1/5$ of the sample was loaded onto a single tungsten filament and analysed using a Finnigan MAT 262 multiple collector mass spectrometer. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios were normalized to a $^{86}\text{Sr}/^{88}\text{Sr}$ ratio of 0.1194. The overall precision of the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio determination is approximately $\pm 10 \cdot 10^{-6}$ (2σ errors). The reproducibility of $^{87}\text{Sr}/^{86}\text{Sr}$ ratio measurement was tested by duplicate analyses of the NBS 987 standard and the mean value obtained during this study was $0.710227 \pm 17 \cdot 10^{-6}$ (2σ ; $n = 70$).

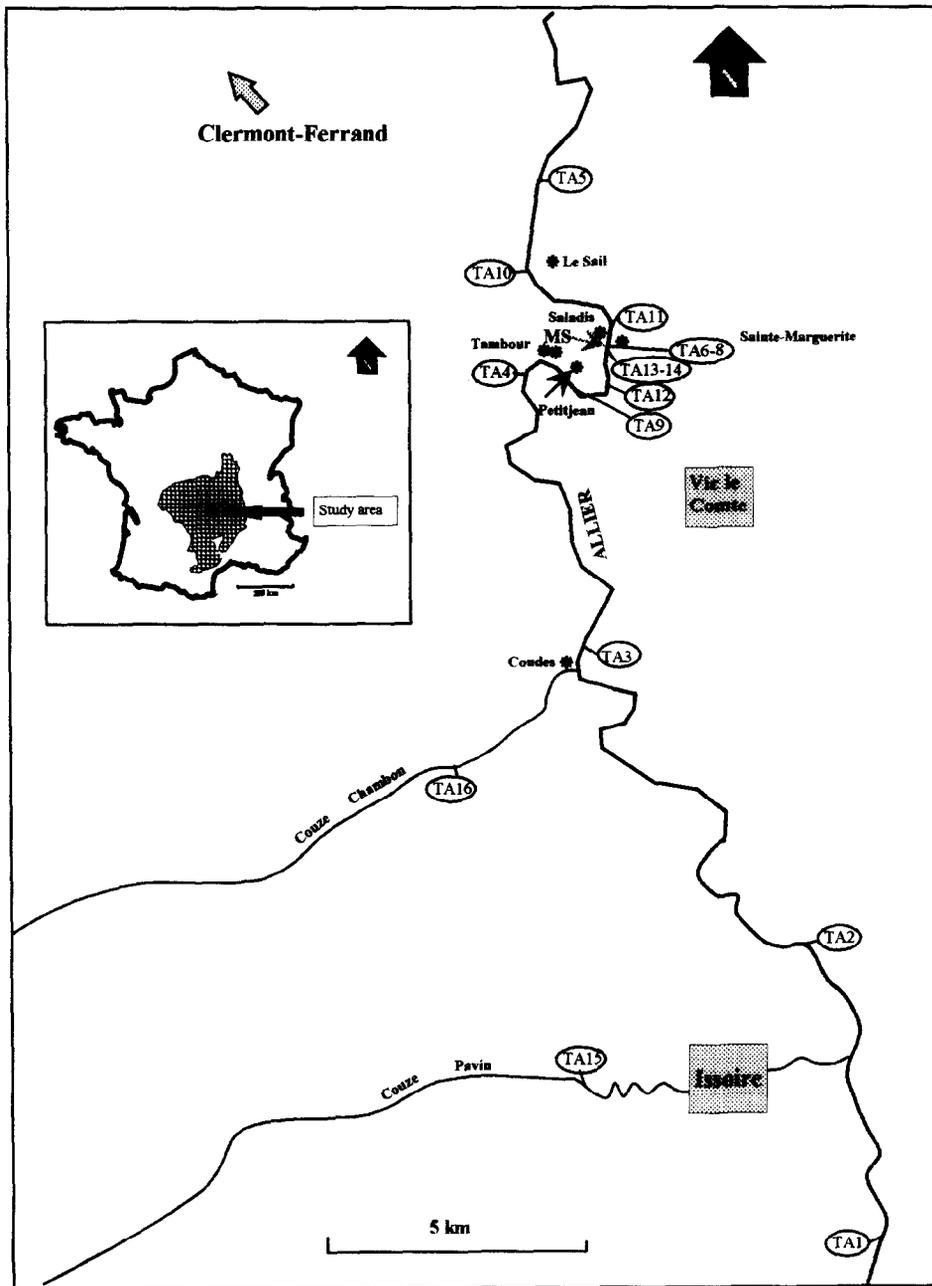


Fig. 1. The sampling site in the Limagne d'Allier. (a) General location of the study area in the Massif Central, France. (b) The Allier River flood plain. TA, sampling points of the spatial study; MS, sampling point of the monthly survey; *, mineral springs.

Table 1

Results of the monthly survey of the Allier River: master variables (discharge, electrical conductivity C , T , pH), major ions (Cl, SO_4 , Ca, Na, Mg, K), trace element (Sr) and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios. Discharge W is expressed in m^3/s , electrical conductivity C in $\mu\text{S}/\text{cm}$, T in $^\circ\text{C}$ and all concentrations in mg/l . Chemical and Sr isotope composition of the mineral water end-member are also indicated (data are from Négrel et al., 1997a)

Date	W	C	pH	T	Ca	Na	K	Mg	Cl	SO_4	Sr	$^{87}\text{Sr}/^{86}\text{Sr}$
09/02/94	167	–	–	–	13.9	12.5	2.9	5.1	15.6	12.4	0.10	0.711515
31/03/94	nd	331	6.9	12.9	16.2	38.0	5.0	7.5	35.7	13.1	0.16	0.711791
18/08/94	14	745	7.18	20.9	38.2	128.5	13.4	18.7	107.9	25.2	0.41	0.712656
19/09/94	38	323	7.42	10.9	21.3	39.6	6.6	9.0	27.3	12.4	0.21	0.711524
23/09/94	353	–	–	–	16.6	7.0	4.5	4.8	8.7	11.4	0.11	0.710124
05/10/94	196	207	7.08	12.3	12.4	21.0	3.8	5.6	20.6	12.8	0.14	0.71137
27/10/94	158	155	7.25	10.3	8.9	11.9	2.9	3.4	11.9	9.1	0.10	0.710785
17/11/94	204	141	6.84	10.1	10.7	8.2	2.5	4.0	8.7	11.8	0.09	0.710866
16/12/94	46	290	7.31	5	19.2	29.0	4.5	8.0	27.6	16.6	0.15	0.71155
17/01/95	25.6	159	7.48	4.4	12.1	10.1	3.1	4.8	11.2	12.1	0.09	0.710758
30/01/95	30.7	104	7.36	15.9	6.9	6.4	2.0	2.9	6.9	6.8	0.07	0.709511
06/03/95	27.6	157.65	7.37	5.6	–	–	–	–	9.4	6.9	0.09	0.710384
06/04/95	20.7	203	7.23	17.9	13.2	24.3	4.5	5.8	18.7	9.4	0.16	0.711142
16/05/95	58	261	7.06	14.8	14.1	31.1	4.7	6.3	16.6	–	0.17	0.711771
15/06/95	28.6	211	7.56	19.3	28.7	58.0	7.7	10.3	38.6	12.4	0.24	0.711839
Mineral water end member					270	1350	160	130	1340	100	6.5	0.7134

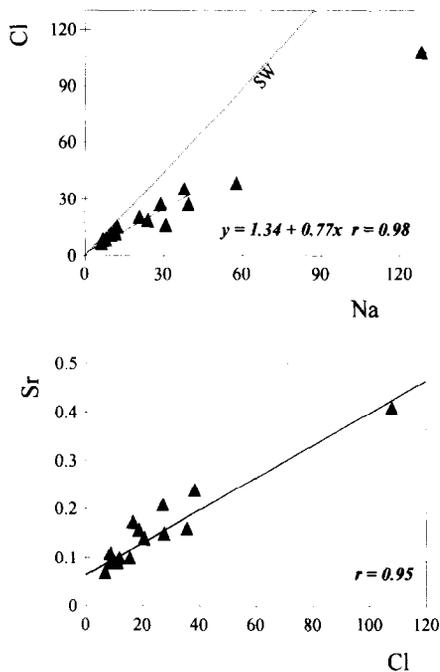


Fig. 2. Binary relationships (a) Cl vs. Na and (b) Cl vs. Sr for the monthly samples of the Allier River. Dotted line, sea water; solid lines, linear correlation.

3. Results and discussion

3.1. Monthly study of the Allier river

3.1.1. Chemical and isotopic characterization of Allier river water

The master variables, chemical composition and Sr isotope content are summarized in Table 1. The discharge of the Allier River over the period studied ranged between 14 and $353 \text{ m}^3/\text{s}$. The highest discharge was measured in winter and spring, and base flow conditions were observed in summer. The hydrograph for the studied period is illustrated in Fig. 3.

Generally, variations in the chemical composition of the dissolved load carried by a river can be studied through relationships between electrical conductivity and discharge (Meybeck, 1986). The greater the discharge, the more diluted the water and the lower the electrical conductivity. However, since the sampling site is located in the mineral water seepage area, no relationship exists between these two parameters (Table 1). No correlation is observed between the concentration of major elements and discharge; the correlation coefficient between these two parameters

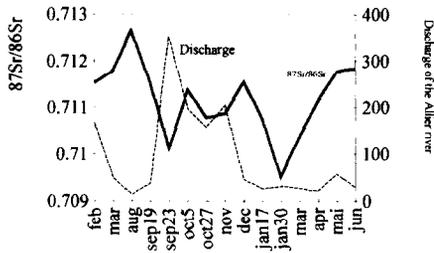


Fig. 3. Plot of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (solid line) and discharge (dotted line, data are from the French Department of Public Works) of the Allier River during the monthly survey as a function of the sampling periods.

is rarely significant. Nevertheless, high concentrations are recorded for August, corresponding with the lowest discharge of the river, and relatively small concentration fluctuations are observed during various water stages.

Binary correlations exist between chemical elements because the correlation coefficients are always significant. The relationships between Cl and Na concentrations and between Cl and Sr concentrations are illustrated in Fig. 2a and b, respectively. In the Cl vs. Na graph, all the river water samples lie to the right of the sea water line. This indicates an excess of Na over Cl, generally related to the dissolution of Na-rich feldspar in such granitic environments (Comans et al., 1987). The Cl vs. Sr relationship is similar to that of Cl and Na. These relationships suggest the existence of two end-members, one with high and the other with low concentrations.

$^{87}\text{Sr}/^{86}\text{Sr}$ ratios vary between 0.709511 (January 1995) and 0.712656 (August 1994) (Fig. 3). The highest Sr isotopic composition is observed during the low flow stage in August, although a low $^{87}\text{Sr}/^{86}\text{Sr}$ ratio is also observed during a low flow stage (January 30). The lack of correlation between both $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and discharge and between the major elements and discharge may reflect the influence of the sampling location. Indeed, the existence of numerous mineral springs in the Allier streambed might cause a shift in this type of relationship.

There is a good correlation between $^{87}\text{Sr}/^{86}\text{Sr}$ and $1/\text{Sr}$ ratios (Fig. 4) with a regression line $^{87}\text{Sr}/^{86}\text{Sr} = 0.71289 - 0.0002 1/\text{Sr}$ and a coefficient correlation $R = 0.88$. This relationship clearly indicates binary mixing between two end-members (Faure, 1986; Négre et al., 1997b). In the Allier River valley, the $^{87}\text{Sr}/^{86}\text{Sr}$ vs $1/\text{Sr}$

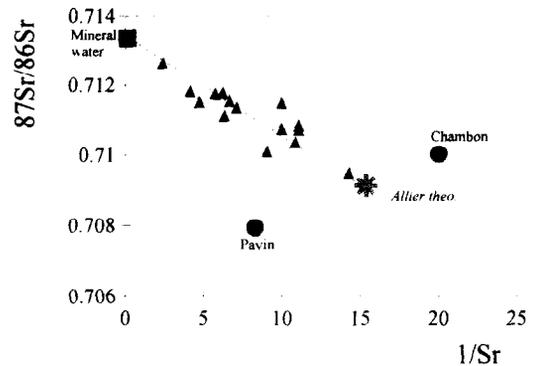


Fig. 4. Relationship between $^{87}\text{Sr}/^{86}\text{Sr}$ and $1/\text{Sr}$ ratios of the monthly samples of the Allier River. Samples of the two tributaries in the sampling area (Couze Pavin and Couze Chambon), and the theoretical Allier River end-member are also represented.

relationship clearly indicates the existence of at least two end-members which control Sr variations in the river. The most concentrated end-member is the most radiogenic (i.e. higher ^{87}Sr) and the most dilute end-member exhibits the lowest isotopic signature.

The descriptive study of monthly variations in Allier River water geochemistry shows that there are two components, one concentrated and radiogenic which could be related to mineral water input, and the other dilute and less radiogenic which could be related to the Allier River water *sensu-stricto*.

The main chemical and isotopic characteristics of the mineral water end-member are summarized in Table 1 (data are from Négre et al., 1997a). Briefly, the 10 mineral water springs sampled in the Limagne d'Allier have a small range of both concentrations and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios. Furthermore, one spring which was studied over 20 months did not have a wide range of Sr isotopic ratios (Négre et al., 1997a). The chemical and isotopic characterization of the mineral water can be, therefore, considered as constant. The average mineral water with a $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.71336 and a Sr concentration of 6.5 mg/l is coherent with the concentrated and radiogenic end-member (Fig. 4).

In order to characterize the pure Allier River end-member, two points were added to the $^{87}\text{Sr}/^{86}\text{Sr}$ vs $1/\text{Sr}$ graph (Fig. 4). They represent samples from the two tributaries of the Allier River in this area, the Couze Chambon and the Couze Pavin (Fig. 1b), sampled upstream of their confluence with the Allier River. The Couze Pavin has the lowest $^{87}\text{Sr}/^{86}\text{Sr}$ ratio

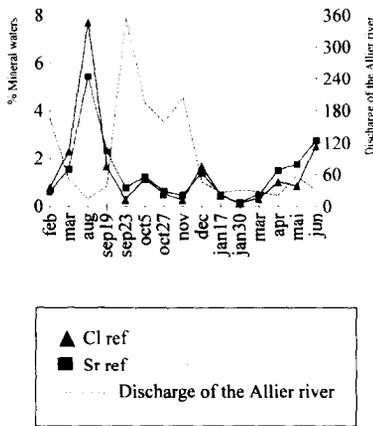


Fig. 5. Plot of the percentage of mineral water input into the Allier River using the Sr reference (squares) and Cl reference (triangles) during the monthly survey as a function of the sampling periods. The discharge of the Allier River (dotted line) is also represented.

(0.707938) and the highest Sr content (0.12 mg/l). The Couze Chambon has a Sr content of approximately 0.05 mg/l but a lower Sr isotope composition (0.710039). A theoretical Allier end-member is symbolized on the graph; it corresponds to a mixing of the Allier River water, upstream from the confluences with the Couze Pavin and Couze Chambon, and the water from the two tributaries. Its position must be on the linear relationship; its $^{87}\text{Sr}/^{86}\text{Sr}$ ratio is estimated to be about 0.709, and the Sr content approximately 0.06 mg/l.

3.1.2. Modelling Allier river variations

Mixing processes can be studied with Sr isotope systematics using the binary mixing equation described for the mixture of surface and mineral waters in Négrel et al. (1997b). The two end-members are the Allier River water (*sensu-stricto*) and the mineral water. The binary mixing equation is:

$$^{87}\text{Sr}/^{86}\text{Sr}_m \times [\text{Sr}]_m = (^{87}\text{Sr}/^{86}\text{Sr}_1 \times [\text{Sr}]_1) + (1-f)(^{87}\text{Sr}/^{86}\text{Sr}_2 \times [\text{Sr}]_2) \quad (1)$$

where $(^{87}\text{Sr}/^{86}\text{Sr})_m$ is the measured isotopic ratio in the mixture, $(^{87}\text{Sr}/^{86}\text{Sr})_1$ and $(^{87}\text{Sr}/^{86}\text{Sr})_2$ are the isotope ratios of the first and second end-members, respectively, and $[\text{Sr}]_m$, $[\text{Sr}]_1$, and $[\text{Sr}]_2$ are the Sr concentrations of the mixture, and the first and second end-members, respectively. The mixing parameter is represented by $\frac{[\text{Sr}]_1}{[\text{Sr}]_1 + [\text{Sr}]_2}$ and $1-f$ corresponds to $\frac{[\text{Sr}]_2}{[\text{Sr}]_1 + [\text{Sr}]_2}$.

Mixing can also be described by a binary mixing equation using a conservative species such as Cl and a mass balance equation (Plummer and Back, 1980; Pauwels et al., 1992; Bertin and Bourg, 1994). Cl varies very little in the mineral waters of interest, with a concentration around 1340 mg/l (Négrel et al., 1997a). The Cl mixing equation is:

$$[\text{Cl}]_m = f[\text{Cl}]_1 + (1-f)[\text{Cl}]_2 \quad (2)$$

where $[\text{Cl}]_m$, $[\text{Cl}]_1$, and $[\text{Cl}]_2$ are the Cl content of the mixture, and the first and second end-members, respectively, the mixing parameter f is represented by $\frac{[\text{Cl}]_1}{[\text{Cl}]_1 + [\text{Cl}]_2}$ and $1-f$ by $\frac{[\text{Cl}]_2}{[\text{Cl}]_1 + [\text{Cl}]_2}$.

To apply Eqs. (1) and (2), the two end-members must be characterized. The Allier River and the mineral water end-members have been described in the previous paragraph and the values are used in the calculation of Eq. (1).

The Cl content of the pure Allier end-member required by Eq. (2) can be estimated by the Cl vs. Sr relationship (Fig. 2b) and gives a Cl content of around 5 mg/l for the theoretical Allier River end-member. This value is less than the lowest Cl content measured in Allier River water during our study period (6.9 mg/l on January 30, 1995).

Eqs. (1) and (2) enabled quantification of the input of mineral water using two different calculations. The results are summarized in Fig. 5 where the two curves (Sr reference and Cl reference) and the discharge of the Allier River are indicated. The highest input of mineral water (>5%) corresponds to the August sample taken during base flow conditions. Except for this one sample, the mineral water input never exceeds 2%. Results of the two computations (Sr isotope systematics and chloride reference) are in good agreement as illustrated by the Cl and Sr reference curves in Fig. 5. The greatest discrepancy between the two calculations is observed for the August sample. Moreover, results show no correlation between mineral water input and river discharge; identical inputs of mineral water can be seen in spite of large discharge variations. This implies that no link exists between hydrological functioning of the river and the input of mineral water. Moreover, the effluent seepage may occur in a part of the channel representing only a small volume of the channel cross-section, meaning that the precise discharge of mineral water into the Allier streambed cannot be estimated.

3.2. Spatial study

The variations in solute concentrations across the river channel were measured at 14 sites representative of areas where; (a) mineral water emerges, (b) no mineral water emerges, and (c) mixing is complete. Cross-sections along the Allier River are referred to as TA x , x being the number of the cross-section ranging from 1 to 16 as illustrated in Fig. 1. For each cross-section, the sample numbered TA x /1 was collected on the right bank and the last number in the sequence (i.e. 3, 4, 5 or 6), corresponds to the sample collected closest to the left bank.

The database of the spatial study is available on request from the senior author. All element concentrations increase downstream. The increase in the total dissolved solutes (TDS) carried by the river is indicated by variations in electrical conductivity which increases from 125 $\mu\text{S}/\text{cm}$ at the first site (TA1) to 200 $\mu\text{S}/\text{cm}$ at the last site (TA5). The electrical conductivity of the two tributaries (Couze Pavin and Couze Chambon) causes an increase from 125 $\mu\text{S}/\text{cm}$ (TA1) to 170 $\mu\text{S}/\text{cm}$ (TA3). Thereafter, the electrical conductivity of the river increases to 200 $\mu\text{S}/\text{cm}$, although there are no other tributaries. This increase can be linked to an input of mineral water seepage in the river bed.

As in the monthly survey, the Cl content of the dissolved load was considered to be a more precise reference than conductivity. Fig. 6(a)–(n) show the 14 sites and the samples collected at each site. A detailed study of Cl content variations across the Allier channel reveals two types of behaviour. Certain cross-sections (TA1–4) show weak variations in Cl content between the right and left banks, whereas others (TA6–9, 13, 14) show large variations.

The first group (cross-sections TA1–4) have a coefficient of variation (CV) of less than 2% but the Cl content of the river water increases from TA1 (mean Cl content: 7.97 mg/l) to TA4 (mean Cl content: 11.66 mg/l); this increase can be attributed to input of the two tributaries – the Couze Pavin (Cl content: 12.90 mg/l) which flows into the Allier between cross-sections TA1 and TA2, and the Couze Chambon (Cl content: 19.05 mg/l) which joins the Allier between cross-sections TA2 and TA3. The Cl content in cross-sections TA1 to TA4 is also higher on the right bank than on the left bank, which is certainly a result of the lack of complete mixing in the Allier channel.

Within the second group, cross-section TA9 have a CV of around 12% between the right and left banks, which cannot be attributed to the Tambour and Petitjean springs as they emerge on the left bank. Variations from one bank to the other are certainly due to effluent seepage from springs located in the Allier streambed near the middle of the channel. The Cl concentrations of the next cross-section (TA12) are very similar. The difference between samples collected near the two banks is around 1.4%, and only around 1% for the other three samples of the cross-section TA12 whereas the uncertainty of the Cl measurement reaches 3%. At the TA12 location, therefore, the Allier water mass is the same across the channel and mixing can be assumed to be complete.

Cross-sections TA6–8, 13 and 14 are located in the area of Saladis-Sainte Marguerite where mineral springs emerge on both the left and right banks of the river (Fig. 1b). Cross-sections TA14, 13, 8 and 7 (Fig. 6(g), (h), (j), (k)) have similar trends in Cl content variability across the channel with the highest Cl content always measured on the right bank. TA6 (Fig. 6i), however, does not show a similar pattern in spite of its location between TA13 and TA7; the Cl content decreases by 9.1% between point 1 on the right bank and point 4, and then increases by 6.4% between points 4 and 5, possibly corresponding to an input of mineral water near the right and left banks.

The decrease in Cl content between points 1 and 2 in cross-sections TA14, 13, 8 and 7 ranges from 73% (TA13, Fig. 6h) to 18% (TA14, Fig. 6g). This may be related to the Sainte Marguerite mineral springs (Fig. 1b). A more detailed examination of Cl concentrations (with the exception of point 1 shows a steady pattern for TA14 (Fig. 6h), and a slight decrease (3–5%) between points 2 and 4 and a slight increase up to point 5 for TA13 (Fig. 6g). These variations are, however, insignificant compared to the reproducibility of the Cl analyses (better than 5%).

At TA7 (Fig. 6j), Cl decreases significantly (13%) between points 2 and 4. Here, the input of mineral water occurs over a larger area of the streambed than at TA14 and TA13. At TA8 (Fig. 6k), Cl increases and decreases repeatedly and no trend is observed between points 2 and 5. At TA6 (Fig. 6i), the trend between points 2 and 5 is fairly similar to that observed for TA13 and TA7 (Fig. 6h and j). The

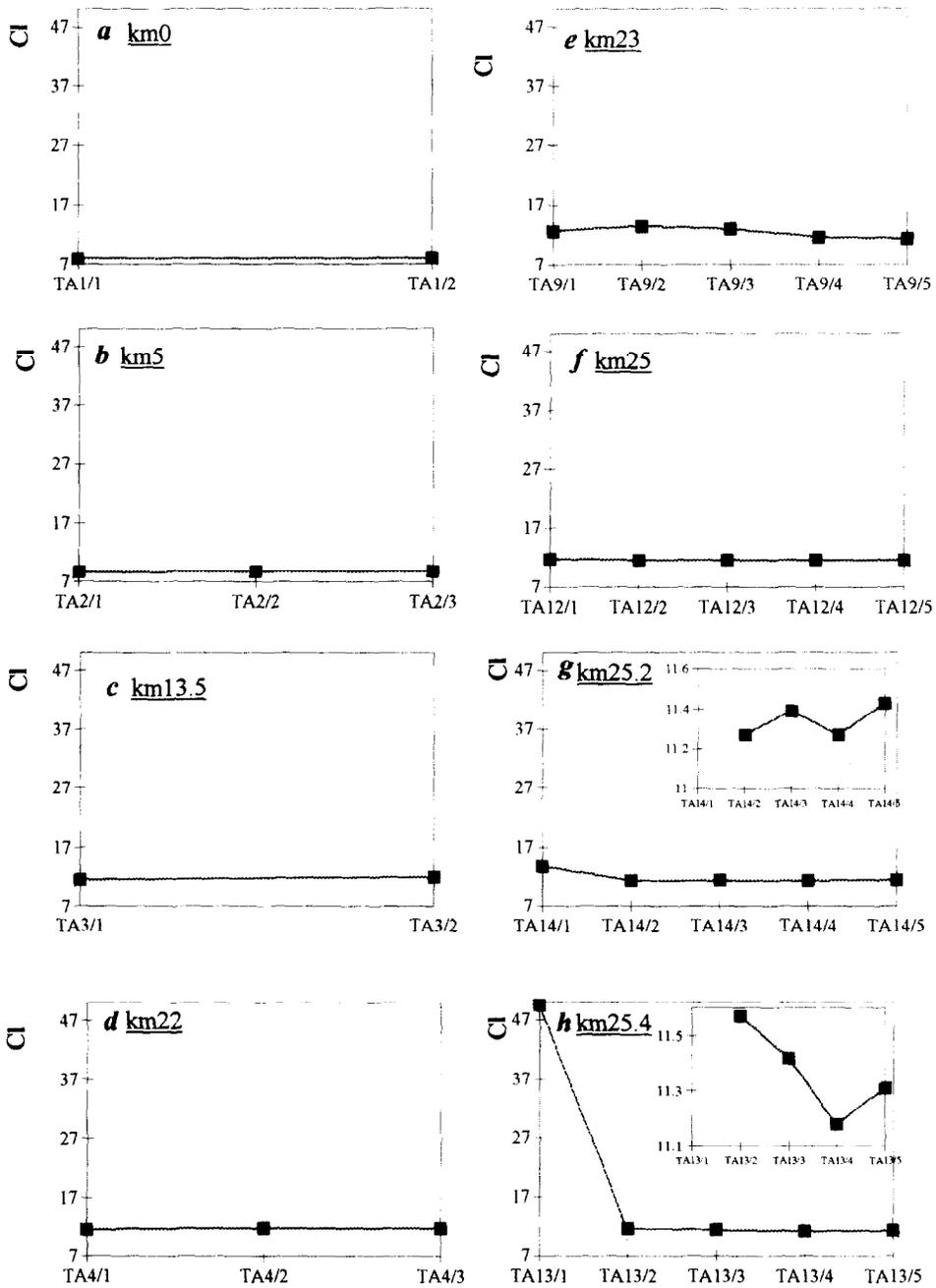


Fig. 6.

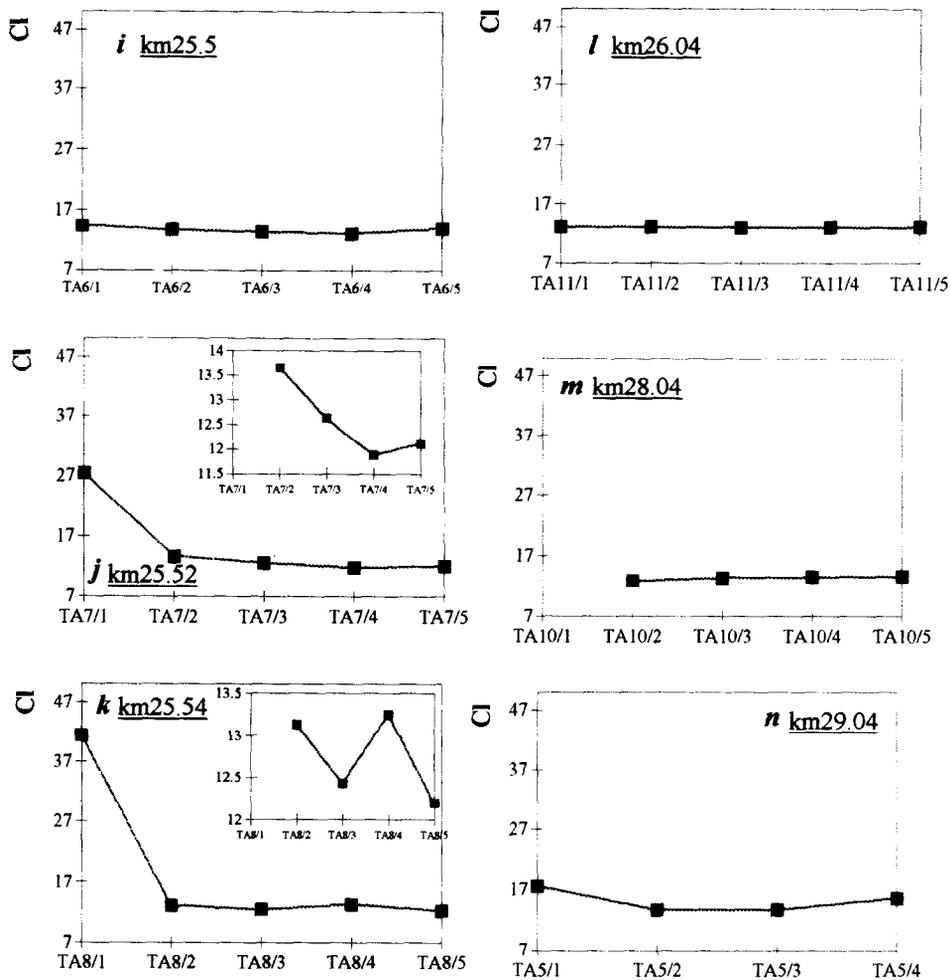


Fig. 6. Plots of the Cl concentrations of the Allier River for the 14 channel cross-sections of the spatial study. Sample 1 refers to the sample collected near the right bank and samples noted 3, 4 or 5 refer to those collected near the left bank. The distance from point zero (see Fig. 1(a)) is indicated on each graph.

next cross-section (TA11, Fig. 6l) is directly downstream of the Saladis-Sainte Marguerite mineral springs and the trend of Cl values between the right and left banks is constant (the divergence is less than 0.3%, and therefore insignificant).

Cross-sections TA10 and TA5 (Fig. 6m and n) are located near the Le Sail spring and the Cl content at TA10 increases 6% from the right to the left bank, whereas at TA5, the lowest Cl content is measured in the middle of the channel, and increases by 22 and 11% towards the right and left banks, respectively. The two trends observed for

TA10 and TA5 could be related to mineral water springs in this area.

3.3. General mass balance in the Allier river

The increase in Cl content between TA1 and TA3 is related to the confluence of the Allier River and its tributaries the Couze Pavin and the Couze Chambon. The discharge of these rivers has not been measured but, based on field observation of their depth and width, we can estimate that they represent, respectively, an input of around 12 and 10% of the discharge of the Allier

River just upstream of the confluences. A binary mixing calculation for the tributaries and the river gives a Cl content of 8.6 mg/l downstream of the confluence with the Couze Pavin. Cl content measured at TA2 ranges from 8.65 to 8.8 mg/l and is, therefore, in agreement with this calculation. Similar calculations for mixing of the Couze Chambon and the Allier waters (river water represented by the mean value at TA2) give a Cl content in the river after mixing of around 9.8 mg/l which is lower than the mean value observed at TA3 (11.66 mg/l). This difference could be related to an input of mineral water directly into the Allier streambed. Indeed, near the Allier channel, the Coudes spring (tapped in the village, Fig. 1b) has a Cl content of 356 mg/l (Négrel et al., 1997a). If we assume there is mixing downstream of the confluence with the Couze Chambon (Cl = 9.8 mg/l) between the river water and a mineral water end-member, the Cl content could be as great as 11.66 mg/l.

Between TA3 and TA4 (Fig. 6c and d), the mean Cl content does not vary and the value of 9.8 mg/l for the river water can be assumed to represent the Allier end-member upstream of the Saladis-Sainte Marguerite mineral springs.

A model similar to that developed for the monthly study using Cl as a reference was applied to the spatial survey using equation (2). The Allier end-member is characterized by a Cl content of 9.8 mg/l and results show that direct mineral water input into the Allier streambed ranges from 0.1 to 0.15% for most of the samples (TA3, 4, 7, 9, 14, 13) and is greater than 2% in samples TA8/1 and TA13/1. In sample TA7/1, this input is about 1%.

The chemical composition of mineral water in the Limagne d'Allier shows little variation (Négrel et al., 1997a) and for each element, the proportion of mineral water can be calculated using the content of the element in the river water, the percentage of Cl resulting from the previous calculation and the X/Cl ratio of the mineral water end-member, X being the chemical element. This calculation was done for SO₄, Ca, Na, K, Mg and Sr; general mass balance was calculated by:

$$\phi MW = \Sigma(X^+, X^-) \text{ and } Al = (X^+, X^-) \quad (3)$$

where MW and Al are the proportions of mineral water and Allier River water *sensu-stricto*, respectively, using the sum (X⁺, X⁻) of cations (Ca, Na, Mg, K, Sr) and anions (SO₄ and Cl).

The trends of MW along the various cross-sections

reflect the Cl patterns seen in Fig. 6. For example, at TA11 (Fig. 6l), variations in Cl content are as great as 0.3% and the range of MW is 0.132 to 0.135% with a mean value of 0.134%. The input of mineral water into the Allier streambed can be determined at this cross-section because it is the point nearest to the Allier gauging station. The discharge of the river at the gauging station was 17.7 m³/s during the sampling period, leading to an input of mineral water of around 0.02 m³/s in the Allier channel.

4. Conclusion

Geochemical tools such as major ions and Sr isotopes can be used in a complementary manner to characterize and quantify the input of mineral water in a stream flow. Geochemical modelling using conservative species has made it possible to calculate an input of around 0.02 m³/s for the mineral water end-members during low flow stage of the Allier River. Sr isotopes can now be used as a complementary tool in order to validate the input of mineral water through its isotopic signature, which may be different from that of other possible sources such as pollution.

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