

## **Dynamic and origin of trace elements in a Mediterranean river (la Peyne)—relations to lithology, discharge, and agricultural practices**

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**Abstract** The variations of dissolved major and trace element concentrations reveal that the Peyne River is affected by lithology and by anthropogenic activity. The influence of evaporites is clearly reflected by the increase of  $\text{SO}_4^{2-}$ , Li and Sr downstream of the Triassic formations. During the rising stage of a flood event the decreasing trend of  $\text{NO}_3^-$  reflects the dilution of sewage treatment plant inputs, whereas the increase of Cu, As, Pb, K, and to a lesser extent Zn, attests to their release from soil. At the peak discharge, the high concentrations of Cu and As (reaching 12.7, 6.8 and 0.699  $\mu\text{g l}^{-1}$ , respectively) indicate a significant impact of the fungicides used for vine treatment. In base flow conditions and in groundwater it seems that the impact of vine treatment is negligible.

**Key words** anthropogenic influence; lithology; metals and arsenic; nitrate; small Mediterranean basin; vine treatment

### **INTRODUCTION**

Although trace metals are toxic for humans and aquatic ecosystems, the processes controlling their concentrations and fate in rivers remain poorly understood (Sherrell & Ross, 1999). Indeed, most of the available fluvial time series data are erroneous due to contamination during sampling and analysis (Shiller 1985; Benoit, 1994). This situation has led to the invalidation of most data sets obtained in the framework of national monitoring networks (Windom *et al.*, 1991).

In Mediterranean regions, time-series of trace metal concentrations are reported for the Rhone River (Elbaz-Poulichet *et al.*, 1996), the Vene River (Luck & Ben-Othman, 1998) and runoff waters (Ribolzi *et al.*, 2001). Although the typical Mediterranean basins represent altogether more than 50% of the inputs to the Mediterranean Sea, they have been poorly studied. These basins are small (50 to 2000  $\text{km}^2$ ) and display an intermittent functioning in relation to the Mediterranean climate, which alternates between long drought periods and short but intensive rainy events. In these basins, the majority of the annual transport occurs in less than three months (Meybeck *et al.*, 1994). Because they constitute an important water resource and a potential source of pollution for the Mediterranean Sea, a better knowledge of the processes controlling their metal concentrations and fluxes is necessary.

This study presents preliminary data obtained in the Peyne River basin. This typical Mediterranean basin is strongly affected by the intensive use of arsenic and copper fungicides for vine culture.

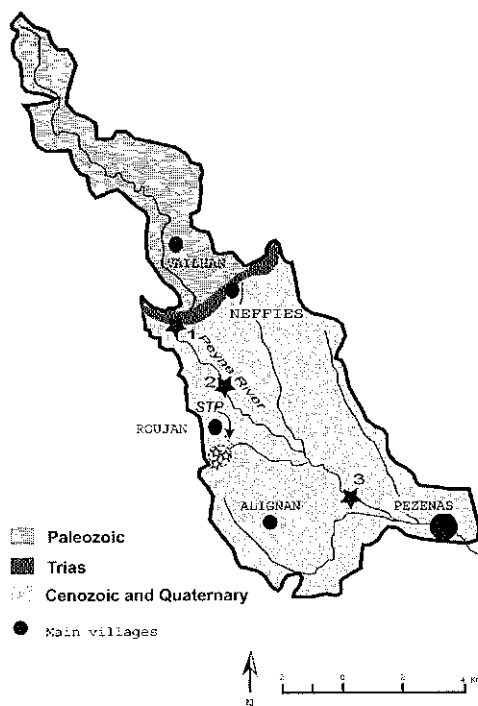
Major ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{HCO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ) and trace (Li, Sr, Cu, Zn, Pb, As and U) element concentrations have been determined in base flow conditions and during a flood event. The aim was to better understand the respective influence of natural and human factors, and the mechanisms controlling the dynamic of trace metals, especially As and Cu.

## METHODS

### Site description

The Peyne River basin covers a surface of 117 km<sup>2</sup> in southern France (Fig. 1). The basin is composed of three geological entities with contrasting lithologies.

The northern part of the watershed corresponds to the Paleozoic basement which includes thrust units of Ordovician to Visean age and which belongs to the southernmost part of the Variscan belt (Montagne Noire). The basement lithologies include sandstones and bituminous shales. A thin Triassic cover lies unconformably on the basement. It mainly comprises sandstones, marls and evaporitic layers (anhydrite



**Fig. 1** Sketch geological map of the Peyne River basin showing locations of the sampling stations. Filled stars: river stations; open stars: groundwater. STP: sewage treatment plants.

and gypsum). The southern and main part of the watershed is constituted of Miocene deposits (marine sands and marls) and Quaternary alluvial deposits (gravels and sands).

The mean annual precipitation on the basin is 650 mm, with a seasonal distribution typical of the Mediterranean climate, including long drought periods and strong rainy events, in spring and autumn generally.

The upper part of the basin still remains little affected by human activity and is mainly covered by a typical vegetation of Mediterranean landscape, while in the lower part (downstream station 2, Fig. 1) more densely populated, intensive vine culture prevails.

### Sampling

The locations of sampling stations are shown in Fig. 1. Three surveys have been carried out in base flow conditions (July 2001 and March 2002) and during a flood (October 2001). In base flow, samples were taken by hand; flood samples were recovered using an automatic sampler (Sigma 800SL). Groundwater samples were collected using a hand pump in three tube wells of the Roujan basin (Fig. 1) during base flow conditions

The water was filtered through 0.22  $\mu\text{m}$ -pore size acid-washed Millipore PVDF membranes mounted in polycarbonate Sartorius filtration units. The filtration was carried out under a class 100 laminar flow hood providing a clean environment. The filtered samples acidified ( $\text{pH} = 2$ ) with Merck Suprapur  $\text{HNO}_3$ , were stored in acid pre-cleaned polyethylene bottles until analysis.

### Analysis

Alkalinity was measured using acid titration. Other major ions were determined using capillary electrophoresis.

Trace elements, with the exception of Fe and As in the dissolved phase, were analysed by ICP-MS (VG-PlasmaQuad-PQ 2+). The calibration of the ICP-MS was performed by calibrating peak intensity, acquired in peak jump mode with standard solutions.  $^{115}\text{In}$  and  $^{209}\text{Bi}$  were used as internal standards to correct for changes in peak intensities due to instrumental drift and matrix suppression.

Arsenic in the dissolved phase was determined using a hydride generation system coupled to an atomic fluorescence. The method is similar to that described by Andreae (1977), but was modified according to Branch *et al.* (1991). It involves a reduction with potassium iodide in the presence of ascorbic acid and production of arsine by reaction with  $\text{NaBH}_4$ .

Fe was determined using graphite furnace atomic absorption spectrophotometry.

## RESULTS

Data are reported in Table 1. The waters are basic with pH values of between 7.6 and 8. The dominant cation is  $\text{Ca}^{2+}$  and the dominant anions:  $\text{SO}_4^{2-}$  and  $\text{HCO}_3^-$  in

**Table 1** Major and trace element concentrations in the Peyne River in base flow conditions.  $\Sigma^+$  sum of major cations.

Station	date	Major element (meq l <sup>-1</sup> )										Trace elements (µg l <sup>-1</sup> )						
		$\Sigma^+$	pH	HCO <sub>3</sub> <sup>-</sup>	Cl <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Na <sup>+</sup>	K <sup>+</sup>	Li	Cu	Zn	As	Sr	Pb	U
1	July 2001	4.43	8.01	2.88	0.54	<dl	1.02	2.67	1.26	0.46	0.03	2.52	1.62	1.21	0.86	145	0.03	0.49
2	July 2001	10.41	7.74	4.42	0.76	<dl	5.39	7.08	2.56	0.77	0.00	13.07	1.27	2.58	0.68	1109	0.06	1.04
2	April 2002	12.44	7.58	4.13	0.71	0.00	6.63	8.38	3.18	0.78	0.11	14.18	0.56	1.47	0.33	1500	0.01	1.20
3	July 2001	11.25	7.92	5.38	1.68	0.18	4.16	7.73	2.28	1.21	0.04	6.96	1.62	3.18	2.58	584	0.07	1.14
3	April 2002	11.87	7.60	5.57	1.54	0.07	3.42	7.96	2.39	1.38	0.13	5.69	1.02	3.74	1.45	516	0.05	1.15
GW 1	April 2002	14.82	na	7.62	2.21	0.00	3.46	11.11	2.43	1.26	0.01	5.99	3.75	na	0.15	358	na	2.01
GW 2	April 2002	12.90	na	7.10	1.48	0.04	3.13	9.86	1.91	1.13	0.01	4.93	3.98	na	0.10	290	na	1.35
GW 3	April 2002	11.91	na	6.60	1.43	0.25	2.66	9.91	1.04	0.95	0.01	5.15	4.68	na	0.07	210	na	1.15
World average*												1.50	0.60	1.70			0.03	

dl: detection limit; na: not available; \* World average (Martin & Windom, 1991)

equivalent proportions. The water chemistry is highly variable according to flow conditions.

In base flow conditions, each of the three river stations is clearly recognizable from its chemical composition. With the exception of Cu, which displays an erratic distribution, the concentrations of major and trace elements vary along the river and three types of evolutions are recognized:

- Ca<sup>2+</sup> increases from station 1 to 2 and then stabilises.
- Sr, Li, SO<sub>4</sub><sup>2-</sup> and U increase at station 2 and then decrease.
- Cl<sup>-</sup>, Na<sup>+</sup>, As, and Zn increase regularly and their highest concentrations are recovered at station 3 where NO<sub>3</sub><sup>-</sup> appears.

The concentrations of major and trace elements in the groundwater of the basin of Roujan are except for As and Cu in the same range as those of the Peyne River at station 3 in base flow. On average, Cu and As are three times higher and twenty times lower in the groundwater than in the river, respectively.

During the flood event, pH values drop abruptly from 8.01–8.28 to 7.83 at the beginning and then stabilize (Fig. 2). The major and trace elements show contrasted distributions (Fig. 2). Ca<sup>2+</sup>, Na<sup>+</sup>, Mg<sup>2+</sup>, Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup> and HCO<sub>3</sub><sup>-</sup> decrease during the rising stage, as do Li, Sr and U, while Cu, As, Pb, K, and to a lesser extent Zn, increase. In addition, most elements, especially NO<sub>3</sub><sup>-</sup> and Zn, display peak concentrations at the beginning.

## DISCUSSION

The variability of major and trace element contents according to the sampling station, reveals that the stream is chemically affected by a large number of factors. Among them, the lithology and human activities are dominant.

**Lithology** The Paleozoic shales constitute the main lithology upstream. Its influence is clearly evidenced at station 1 where the river water displays the lowest

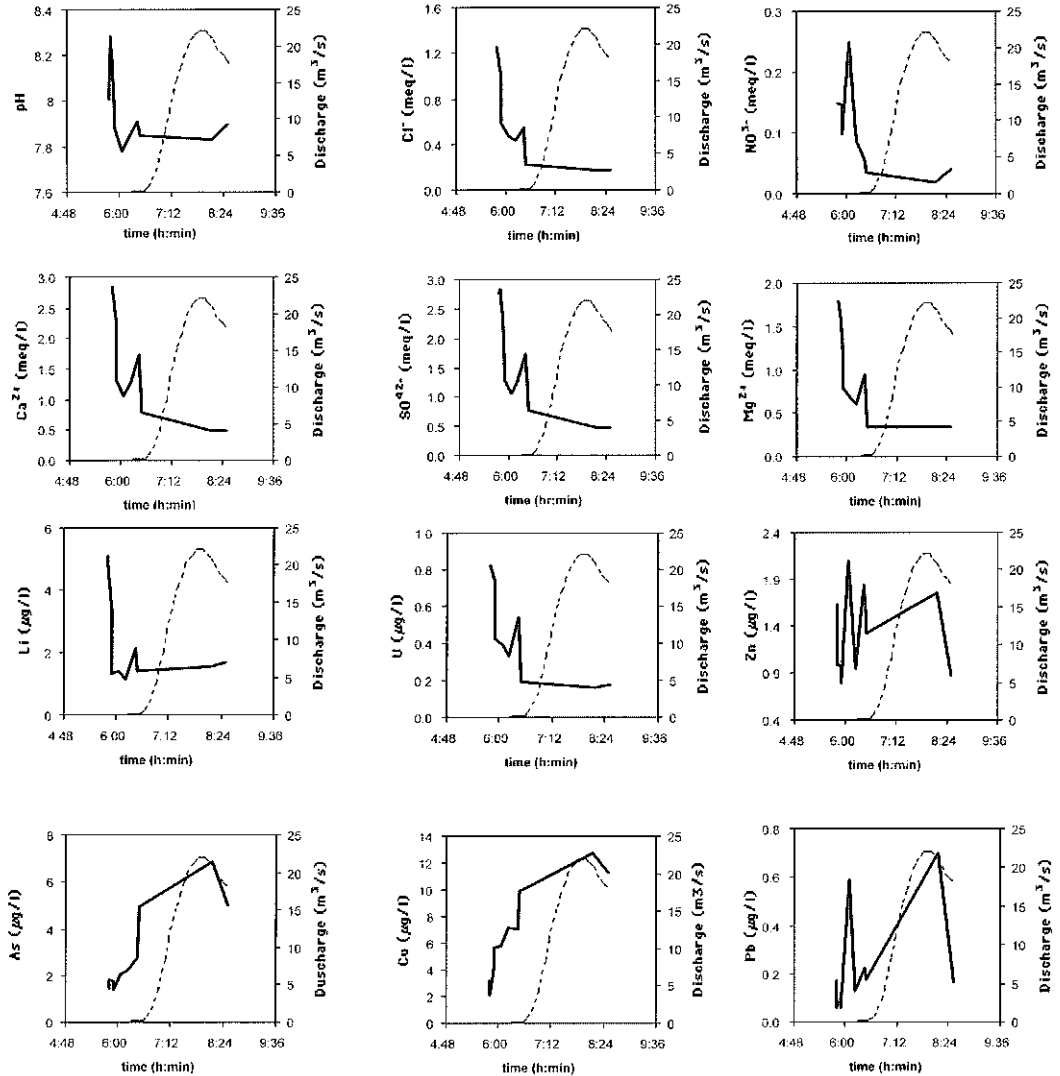


Fig. 2 Distribution of pH, major ion and trace element concentrations at station 3, during the flood event of 20 March 2001.

cation content ( $\Sigma^+ = 4.3 \text{ meq l}^{-1}$ ) and a ratio  $\text{Ca}^{2+}/\text{Na}^+$  close to 6 eq/eq, typical of water draining shales and sandstones (Meybeck, 1986). At station 2, the relative enrichment of the following elements,  $\text{SO}_4^{2-}$ , Li, and Sr is clearly apparent (Fig. 3) and reflects the presence of evaporites in the Triassic formations according to Petelet & Ben-Othman (1998).

It is noteworthy that the influence of evaporites is not revealed at station 1 because they are only recognized at depth (Combes & Ledoux, 1992; Aquilina *et al.*, 1997). Their influence, which appears at station 2, indicates the introduction of groundwater downstream of station 1 in the Payne River.

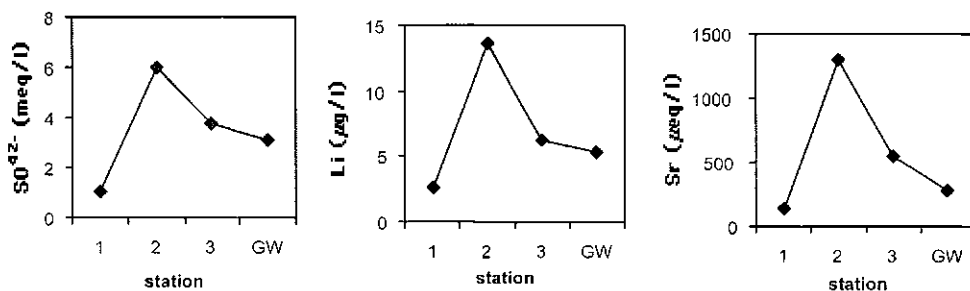


Fig. 3 Spatial variations of  $\text{SO}_4^{2-}$ , Sr and Li concentrations in the Peyne River and in groundwater (GW).

**Human activity** The influence of human activity is evident during the flood event and in base flow conditions at station 3. Two sources of contamination can be distinguished.

Element concentrations and pH during the flood reflect a binary mixing between the base flow and low pH runoff waters (Fig. 2) as recognized elsewhere (Whitfield, 1981; Meybeck, 1986; Driskoll *et al.*, 1987; Shiller & Boyle, 1987; Cook *et al.*, 1994; Seyler & Elbaz-Poulichet, 1996).

During the rising stage the progressive increase of As, Cu, Pb, and to a lesser extent Zn (Fig. 2), suggests their release from soils by overland flow which has been shown to constitute the main contribution during the flood event in the Peyne catchment (Ribolzi *et al.*, 2000; Louchart *et al.*, 2001). Cu, As and Zn undoubtedly originate from the application of pesticides on vine, whereas Pb is generated from atmospheric deposition which still contains gasoline Pb in southern France (Luck & Ben-Othman, 2002).

Surprisingly, the decreasing trend of  $\text{NO}_3^-$  during the rising stage indicates a negligible effect of fertilizers. It reflects the dilution of a point source, which is likely to be a sewage treatment plant.

In base flow conditions the water composition at station 3 reflects that of groundwater, except for As (Table 1). As indicated by the presence of  $\text{NO}_3^-$ , sewage treatment plants (STP) may also partially contribute to the contamination of the river in base flow conditions at station 3. Indeed STP discharges very often dominate the flow in small Mediterranean rivers during dry periods (Elbaz-Poulichet *et al.*, 2002). Their influence may also account for peak concentrations which are particularly important for Zn. Such peaks are generally attributed to flushing of point sources (van der Weijden & Middelburg, 1989; Yang & Sanudo-Wilhelmy 1998) in relation to human activity.

Finally, compared to the world average (Table 1), Cu, As and Pb are similar, whereas Zn is higher. The contamination becomes drastic during flood events where Cu, As and Pb released from the soil surface increase by a factor 4 to 5, reflecting a significant contamination of the Peyne River.

**Acknowledgements** This study was financed by the ACI-Eau et Usages de l'Eau (French Ministry of Research). Claude Dupuy and Marc Leblanc helped in writing the

manuscript. Pascal Brunet and Sandrine Negro are gratefully acknowledged for their assistance in the field.

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