



Naturally dissolved arsenic concentrations in the Alpine/Mediterranean Var River watershed (France)



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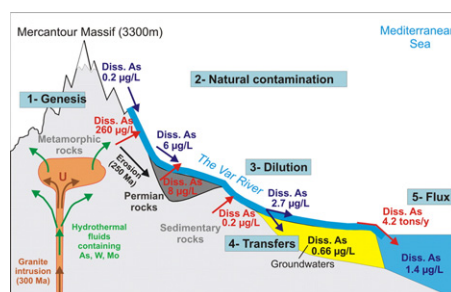
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HIGHLIGHTS

- Variations of dissolved arsenic concentration according to water/rock interactions
- As in river water originates from Permian and Hercynian metamorphic rocks
- 4.2 tons · year⁻¹ of dissolved As is transferred to the Mediterranean Sea.
- The use of a mixing model supports the non-conservative nature of arsenic.

GRAPHICAL ABSTRACT



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ABSTRACT

A detailed study on arsenic (As) in rocks and water from the Var River watershed was undertaken aiming at identifying (i) the origin and the distribution of As in this typical Alpine/Mediterranean basin, and (ii) As input into the Mediterranean Sea. Dissolved As concentrations in the Var River range from 0.1 to 4.5 $\mu\text{g} \cdot \text{L}^{-1}$, due to high hydrological variability and the draining through different geological formations. In the upper part of the Var drainage basin, in the Tinée and the Vésubie valleys, high levels of dissolved As concentrations occur (up to 263 $\mu\text{g} \cdot \text{L}^{-1}$). The two main sources of As in rocks are the Hercynian metamorphic rocks and the Permian argillites. Highly heterogeneous distribution of As in waters draining through metamorphic rocks is probably related to ore deposits containing arsenopyrite. As, U, W and Mo concentrations in water and rocks correspond to the formation of As-rich ore deposits around Argentera granite by hydrothermal fluids deposited at the end of the Hercynian chain formation, which occurred about 300 My ago. In 2009, weekly monitoring was performed on the Var River (15 km upstream of the mouth), highlighting an average dissolved As concentration ($<0.45 \mu\text{m}$) of $2.7 \pm 0.9 \mu\text{g} \cdot \text{L}^{-1}$, which is significantly higher than the world-average baseline for river water ($0.83 \mu\text{g} \cdot \text{L}^{-1}$). Taking the average annual discharge ($49.4 \text{ m}^3 \cdot \text{s}^{-1}$) into account and the As levels in the dissolved phase and in deposits of the Var River, dissolved As input into the Mediterranean Sea would be $4.2 \pm 1.4 \text{ tons} \cdot \text{year}^{-1}$ which represents 59% of the total As flux. This study also reveals a probable non-conservative As behaviour, i.e., possible transfer between aqueous and solid phases, during the mixing of the Var River with a tributary.

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1. Introduction

The metalloid arsenic (As) is usually considered as the prime naturally-occurring carcinogen found in the environment (Nriagu, 2001). Arsenic is a toxic element that poses as an environmental and human threat due to its presence at adverse levels in many surface and ground waters used for domestic consumption (Smedley and Kinniburgh, 2002). Most of the previous studies concerned regions affected by severe As contamination, such as Bangladesh or China (Chakraborti et al., 2010; Fendorf et al., 2010; Michael, 2013; Rodriguez-Lado et al., 2013; Selim Reza et al., 2010). Detailed studies in less contaminated regions are scarce. In many areas of the world, concentrations of As are higher than the WHO drinking water limit of 10 µg/L (Smedley and Kinniburgh, 2002). A better understanding and quantification of the physical and biogeochemical processes governing As transport and mobility in a complex natural system still remain as challenging tasks (Fendorf et al., 2010). When compared to other oxyanion-forming elements, As is among the most problematic in the environment because of its relative mobility over a wide range of pH and redox conditions (Garnier et al., 2010; Katsoyiannis et al., 2007; Masscheleyn et al., 1991; Vink, 1996; Weigand et al., 2010). As mobility depends on water/mineral interactions, they themselves are influenced by the chemistry of the aqueous phase (pH, redox potential, ionic strength and the occurrence of competitive ions, dissolved organic carbon) and by the abundance and characteristics of the solid phases (specific surface, surface charge and crystallinity) (Amstaetter et al., 2009; Bissen and Frimmel, 2003; Grosbois et al., 2011; Haque et al., 2008; Inskeep et al., 2002; Johannesson and Tang, 2009; Oremland and Stolz, 2005; Sharma et al., 2011).

This study concerns the Var River watershed, in the Alpes-Maritimes department, in South Eastern France, where As has never been studied at the level of the drainage basin. This watershed presents local As problems upstream from the basin. For nine villages of the Alpes-Maritimes department, in the upper part of the Tinée or the Vésubie valleys, As concentrations in drinking water are often higher than the European standard of 10 µg · L⁻¹ (monitoring performed by the regional agency of health, ARS). This study focuses on several sampling sites along the main river and several tributaries by means of weekly sampling performed over 1 year. This approach provides a detailed distribution of As throughout the watershed over time which helps in: (i) identifying As origin in rocks and consequently in the water, (ii) determining As fluxes in the whole watershed, and consequently the input into the Mediterranean Sea; and (iii) highlighting a probable non-conservative As behaviour, i.e., transfer between aqueous and solid phases.

2. Local settings

After the Rhône River, the Var River is the second largest river in France (with regard to discharge); it flows into the Mediterranean Sea. The Var River has its source at about 1800 m of altitude. This hydrographic system exhibits both Alpine and Mediterranean characteristics, in the northern and southern areas respectively. Its catchment area is approximately 2820 km² and its annual discharge is about 49.4 m³ · s⁻¹ (34-year monitoring survey in Nice, Pont Napoléon III) at its mouth with the Mediterranean Sea (Fig. 1, data available on the website <http://www.hydro.eaufrance.fr/>). The annual discharge of the Var River greatly varies; it reached 3000 m³ · s⁻¹ during a flood in 1994. In the upper part of the Var River (up to Plan du Var), the main tributaries are the Coulomp, the Cians, the Tinée, the Vésubie and the Estéron rivers (Fig. 1). The Tinée River and the Vésubie River represent a third and a sixth of the annual Var discharge respectively. The lower part of the Var River (down to Plan du Var, hereafter called the Lower Var Valley, Fig. 1) is a 25-km long, wider alluvial plain, representing the main source of drinking water for the Côte d'Azur (>600,000 inhabitants).

The geological characteristics of the drainage basin have been previously described, and only the main features are given here (Féraud et al.,

2009). The north eastern part of the basin consists of Hercynian metamorphic and granitic rocks, through which drain the upper part of the Var watershed via the Tinée and the Vésubie rivers (Fig. 2). Permian sediments, consisting mostly of continental red argillites with some light volcanic layers (rhyolitic cinerites), are located all around the Hercynian massif and in the central part of the drainage basin (north of Puget-Thénier). They are drained by the upper part of the Var, the Roudoule, the Cians and the Tinée rivers and more locally by the Vésubie River. Triassic formations are located close to Permian sediments, in the southern part of the Var watershed. All the rivers drain through sedimentary rocks such as Jurassic, Cretaceous and Tertiary formations which mostly consist of limestone, marls and sandstone. In the Lower Var Valley, there is a Pliocene conglomerate outcrop which is more than 700 m thick.

3. Materials and methods

3.1. Sampling and analytical methods

75 rocks of various types were sampled in the Var River drainage basin (Fig. 2, Table 1). During sampling, only rocks with a degree of alteration were taken, in order to be as representative as possible of the outcrops. Little pieces of rock were cut with a diamond saw and sent to the CRPG laboratory for analysis. Sample preparation and analysis have been previously described (Carignan et al., 2001). All rock samples were digested using alkali fusion. As, Cu, U, W and Mo levels in rocks were measured using an ICP-MS (Thermo Elemental X7). Detection limits were 1.5, 5.0, 0.5, 0.3 and 0.03 mg · kg⁻¹ for ⁷⁵As, ⁶³Cu, ⁹⁸Mo, ¹⁸⁴W and ²³⁸U, respectively.

Water was sampled along the three rivers (Var, Tinée and Vésubie), including their tributaries (Fig. 1). A 15-L plastic bucket, rinsed three times with the water before sampling was used to sample the water, which was taken as far as possible from the river bank. Depending on the sampling date, 11 to 15 sites along the Var River and 6 tributaries were sampled over a distance of 124 km, at altitudes ranging from the sea level to 1570 m (Fig. 1). Water from the output of a power station fed by the Tinée River upstream (called T4 in Fig. 1) was also sampled because it may affect the water quality of the Var River. A weekly sampling in the Var River, on the sampling point VA23, had been performed in 2009 (Fig. 1). Among the six tributaries, this study mainly focussed on the Tinée and the Vésubie rivers because of their importance in terms of discharge and specific chemical composition. 13 to 16 sites along the Tinée River were sampled over a distance of 57 km, at altitudes between 180 m (Var confluence) and 1445 m (Fig. 1). 10 to 12 sites were sampled along the Vésubie River over a distance of 39 km, at altitudes ranging from 150 m (Var confluence) to 1490 m (Fig. 1). Fig. 3 shows variations of the Var discharge upstream from the Var/Tinée confluence (Malaussène) and at the mouth of the river (Pont Napoléon III, Nice) (data available on the website <http://www.hydro.eaufrance.fr/>) according to the sampling dates.

Complementary sampling campaigns were also performed throughout the Tinée River watershed containing both Hercynian granitic and metamorphic rocks. Both river water and spring water used as drinking water were sampled at the La Blache district of the St. Etienne de Tinée village (sampled 24th September 2008 and 28th September 2009) and at the Molières district of the St. Martin Vésubie village (15th and 3rd September 2008 and 2009) (Fig. 1).

For each sampling point, pH, electrical conductivity (EC) and temperature were measured on field, in water samples, with a WTW® field pH-metre. In 2007, these three measurements were not performed. Since 2009, dissolved O₂ has been measured with a Hanna® field O₂-metre. Alkalinity (or HCO₃⁻) was also measured on field with a Hach® titrator kit.

This work focussed only on the dissolved phase of the water (<0.45 µm). Water samples were filtered on field with a single-use syringe through single-use syringe filters (0.45 µm, Minisart® RC25,

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