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Aluminium speciation in the Vienne river on its upstream catchment (Limousin region, France)

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Abstract

The aim of this study was to investigate the speciation of aluminium in the river Vienne on its upstream catchment (Limousin region, France) over a period of seven years (May 1998–September 2004) in order to assess harmful effects on aquatic life. Two sampling points were selected: the first at 4 km from the spring (Peyrelevade), and the second one at 89 km from the spring (Royères). The aluminium speciation was computed with Mineql$^+$ 4.5 speciation software. Organic matter and phosphorous play a major role in aluminium speciation. If we consider the free aluminium ion (Al^{3+}) as being the only toxic form of aluminium, the concentrations of toxic forms recorded at Peyrelevade and Royères were always below the toxic values for fish. However, if the sum of the concentrations of Al^{3+}, $Al(OH)^{2+}$, $Al(OH)_2^+$ and $Al(OH)_4^-$ is taken into consideration, the concentration of aluminium recorded may have adverse effects on aquatic life in the upstream catchment of the river Vienne. $Al(OH)_4^-$ is the major contributor to the concentration in toxic aluminium recorded. In general, $Al(OH)_4^-$ forms appears in water during the summer with water alkalinisation due to an increase in photosynthetic activities.

Keywords: Aluminium; Speciation; Organic matter; Water quality

1. Introduction

Aluminium is one of the most abundant elements in soils and it occurs in soil solution as well as in aquatic systems [1]. Several factors of natural or anthropic origins such as acid rains and atmospheric deposits [2] or the intensive cultivation of spruce and fir [3], have been identified as being responsible for the increase in the concentration of the soluble forms of aluminium in natural water or soils.

A major concern regarding aluminium in the aquatic environment is its potential toxicity in freshwater systems. Dissolved in water, aluminium occurs as many different species with varying toxicity towards aquatic organisms [4]. The most toxic aqueous Al forms [4,5] are Al^{3+} and Al hydroxy species ($Al(OH)^{2+}$, $Al(OH)_2^+$ and $Al(OH)_4^-$), the concentrations in the dominant species are shown to vary with pH, water temperature [6], ionic strength [1,7], inorganic ligands (F^-, SO_4^{2-} and $Si(OH)_4$) [7–9] and organic materials such as humic and fulvic acids [4,7].

In France, many studies have been carried out on experimental catchments of the Vosges and the Ardennes [10] but few data are available on the acidification and the pollution of waters by aluminium in other areas. Only two studies are available on the state of

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contamination of the rivers in the Limousin, [11,12]. These two studies show that some rivers in the Limousin (including the Vienne) display abnormal concentrations of aluminium in their upstream catchments. In the Limousin the presence of aluminium in surface water seems to be due to a combination of natural factors (poor acid brown earth soils, the presence of wet moors and peat bogs) and the intensive cultivation of coniferous trees [12].

In the previous study, no evidence was found to prove that the concentrations in aluminium were potentially harmful to fish in the upstream catchments of the river Vienne [12]. The aim of this study was to investigate the evolution of aluminium speciation as a function of time (1998–2004) in order to better characterize the risk of toxicity for aquatic life.

2. Characteristics of studied catchments

This study was carried out on the upstream catchments of one of the major rivers of the Limousin: the Vienne. Two sampling stations located on its upstream catchment were selected [12]. Table 1 shows the average, minimum and maximum values of the physico-chemical parameters recorded from May 1998 to September 2004 at the 2 sampling stations.

At Peyrelevade the quality of the Vienne water is very good which is very favourable to the growth and survival of salmonids like the fario trout. The reduction in water quality observed at Royère is due to the presence of several small villages and some agricultural pollution (extensive breeding of bovines and sheep).

3. Sampling analyses and computation of Al speciation

Forty and 75 water samples were collected, respectively, at Peyrelevade and Royère over the period May 1998 to September 2004. All physico-chemicals parameters of water samples were determined by the AFNOR methods [13]. The total dissolved aluminium concentrations were measured using a Varian ASS 800 instrument with a graphite furnace and Zeeman correction. Total organic carbon (TOC, used to evaluate the organic matter) analyses were carried out with a Dorhman Phoenix 8000 COT-meter.

Mineql$^+$ version 4.5 was used to compute aluminium speciation at the water temperature recorded on the sampling day. The following species were considered

Table 1
Average, minima and maxima values of different physico-chemicals parameters recorded between May 1998 and September 2004 in the river Vienne upstream catchment

	Vienne (Royères)			Vienne (Peyrelevade)		
	Average	Minimum	Maximum	Average	Minimum	Maximum
Daily average flow ($m^3\ s^{-1}$)	34.3	4.6	148.5	0.27	0.03	1.03
Temperature (°C)	11.6	1.5	23.1	11.6	3.0	22.2
TSS ($mg\ L^{-1}$)	10	1	140	2.8	0.6	9.2
Aluminium ($\mu g\ L^{-1}$)	46.4	16.4	100.6	74.1	22.4	130.5
Aluminium ($\mu mol\ L^{-1}$)	1.72	0.61	3.73	2.75	0.83	4.83
TOC (mg C per L)	3.6	1.7	7.1	3.6	1.7	8.5
TOC (μmol C per L)	300	142	592	300	142	709
pH	6.8	5.8	7.9	6.3	5.7	6.8
Alkalinity - HCO_3^- ($mg\ L^{-1}$)	14	8	26	6	<5	7
Conductivity ($\mu S\ cm^{-1}$)	47	37	63	26	21	31
F^- ($mg\ L^{-1}$)	0.05	0.01	0.14	0.04	0.01	0.09
NO_3^-(NO_3^- $mg\ L^{-1}$)	4.6	2.9	7.0	1.9	1.1	3.2
NO_2^-(NO_2^- $mg\ L^{-1}$)	0.02	<0.01	0.07	0.01	<0.01	0.03
Cl^- (NO_3^- $mg\ L^{-1}$)	4.3	3.5	5.5	4.0	2.8	6.0
SO_4^{2-} ($mg\ L^{-1}$)	2.3	1.8	2.6	1.1	0.5	3.2
NH_4^+(NH_4^+ $mg\ L^{-1}$)	0.05	<0.02	0.12	0.02	<0.02	0.03
PO_4^{3-}(PO_4^{3-} $mg\ L^{-1}$)	0.04	<0.01	0.12	0.04	<0.01	0.18
Total P (P $mg\ L^{-1}$)	0.04	<0.01	0.27	0.03	<0.01	0.08
Si(SiO_3^{2-} $mg\ L^{-1}$)	9	4	15	9	6	22
Ca^{2+} ($mg\ L^{-1}$)	3.1	2.4	3.9	1.5	1.1	1.6
Mg^{2+} ($mg\ L^{-1}$)	1.2	0.9	1.5	0.6	<0.5	0.8
Na^+ ($mg\ L^{-1}$)	4.1	3.4	5	2.9	2.3	3.3
K^+ ($mg\ L^{-1}$)	1.2	0.9	1.8	0.6	<0.5	1.0

TSS: Total suspended solid.
Note that the samples were filtered through 0.45 μm membranes before analysis.

for aluminium speciation: OH^-, F^-, Cl^-, PO_4^{3-}, SO_4^{2-}, $Si(OH)_4$ and organic matter (as mol equivalent of carbon from fulvic acid). Equilibria assumed to be involved in the speciation of aluminium are given in a previous paper [12].

4. Evolution of aluminium speciation as a function of time

Figs. 1 and 2 present the evolution, as a function of time (May 1998–September 2004), of aluminium speciation in the Vienne at Peyrelevade and Royère, respectively. Note that only the main forms with hydroxide, organic matter and phosphorous are shown.

The aluminium ions at Peyrelevade are mainly bound to organic matter (AlFulvates, $AlHPO_4$Fulvates, AlHFulvates) with AlFulvates as the predominant form (Fig. 1). At Peyrelevade, the main forms of aluminium remained fairly constant over the years. It can also be seen that aluminium was mainly bound, simultaneously, to fulvate and phosphate ($AlHPO_4Fulvates^{2-}$). This complex ($AlHPO_4Fulvates^{2-}$) could appear, at the end of summer when the flows are the slower and the water phosphorous content increases slightly due to the rise in the tourist population.

At Royère, aluminium speciation varied rather widely over the years, and this may be due to the change in water composition linked to the presence of diffuse pollution from agriculture or domestic wastewater from small villages (Fig. 2). As at Peyrelevade, the organic matter plays a major role in the speciation of aluminium, but other forms such as $AlPO_4$, $Al(OH)_{3(aq)}$, $Al(OH)^{2+}$, $Al(OH)_4^-$ also appear (>1% of the total forms). During some summers when pH values are above neutral and aluminium water content is lower (close to 15–30 μg L^{-1}), the percentage of the $Al(OH)_4^-$ form of aluminium can reach a significant level (about 10%), (Fig. 2).

5. Assessment of aluminium toxicity for aquatic life

In order to assess the toxicity risk for aquatic life, the evolution of concentrations of toxic forms of aluminium as function of time was investigated. According to the literature, the free aluminium ion (Al^{3+}) [14] or the sum of concentration of Al^{3+}, $Al(OH)^{2+}$, $Al(OH)_2^+$ and $Al(OH)_4^-$, [15] are considered as toxic aluminium forms for aquatic life. The toxic limit concentrations of aluminium are 2.0×10^{-7} mol $L^{-1}$for free Al^{3+} (data obtained for juvenile salmon) [14] and vary from 1.5 to 3.0×10^{-7} mol L^{-1} for the sum of concentrations of Al^{3+}, $Al(OH)^{2+}$, $Al(OH)_2^+$ and $Al(OH)_4^-$ (data obtained for Atlantic salmon) [15].

The Al^{3+} concentrations at Peyrelevade and Royère varied respectively from 3.86×10^{-20} to 1.39×10^{-10} mol L^{-1} and 3.90×10^{-20} to 1.40×10^{-10} mol L^{-1}. According to Roy and Campbell's [14] results, we can assume that aluminium concentrations recorded in the river Vienne upstream catchment do not have harmful effects on aquatic life.

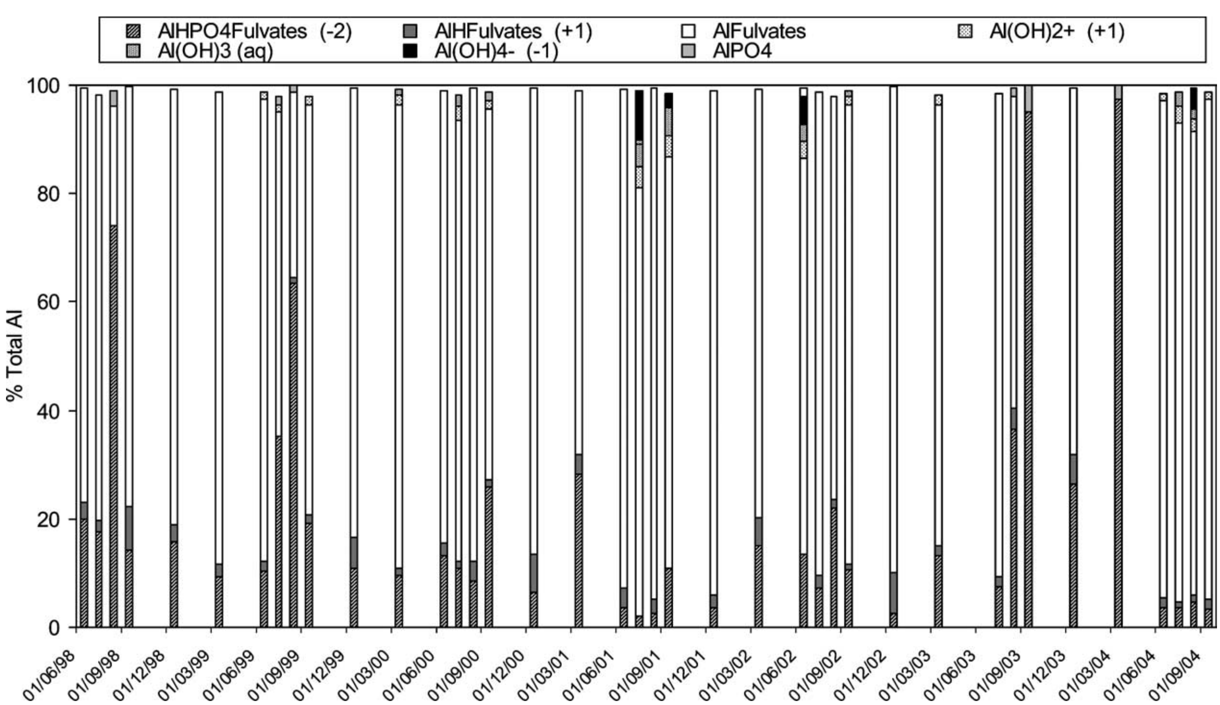

Fig. 1. Evolution of aluminium speciation (only main forms with hydroxide, organic matter and phosphorous are displayed) as a function of time for the Vienne river at Peyrelevade.

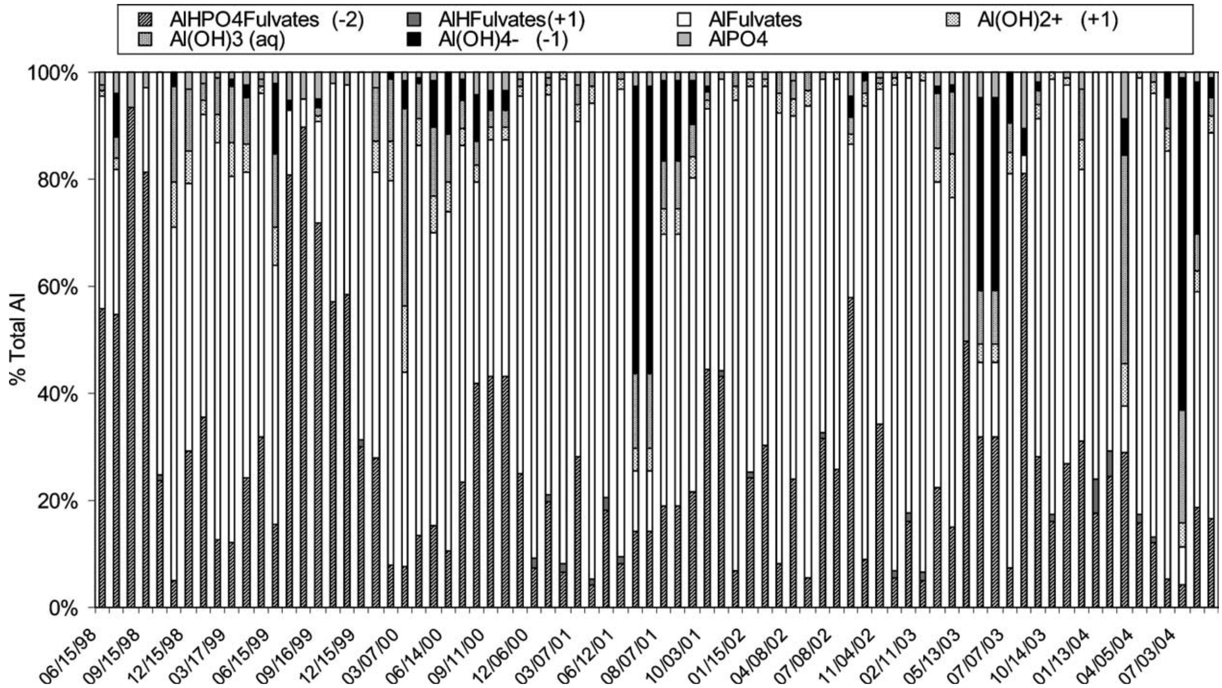

Fig. 2. Evolution of aluminium speciation (only main forms with hydroxide, organic matter and phosphorous are displayed) as a function of time for the Vienne river at Royère.

The conclusions are different if we consider toxic aluminium concentration as the sum of Al^{3+}, $Al(OH)^{2+}$, $Al(OH)_2^+$ and $Al(OH)_4^-$ [15], (Fig. 3). At Peyrelevade, one value for the sum of Al^{3+}, $Al(OH)^{2+}$, $Al(OH)_2^+$ and $Al(OH)_4^-$ is higher than the toxic value proposed by Kroglund and Finstad [15]. At Royère, the values for the sum of Al^{3+}, $Al(OH)^{2+}$, $Al(OH)_2{}^+$ and $Al(OH)_4{}^-$, recorded are eight times (12% of values recorded) higher than the toxic limit proposed by Kroglund and Finstad [15]. Fig. 3 shows that these toxic concentrations seem to appear in summer (June to September) when the concentrations of total dissolved alu-

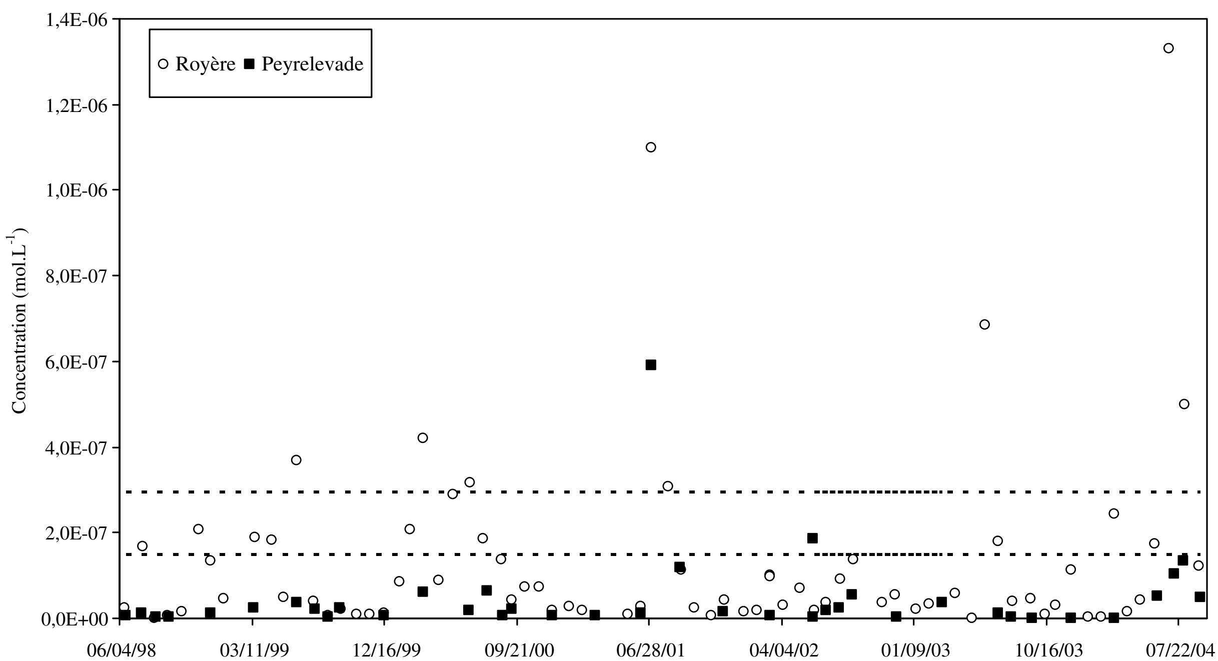

Fig. 3. Evolution of the sum of concentrations of Al^{3+}, $Al(OH)^{2+}$, $Al(OH)_2^+$ and $Al(OH)_4^-$) as a function of time at Peyrelevade and Royère, (- - - area beyond which the sum of the concentrations of aluminium forms is toxic according to Kroglund and Finstad [15]).

minium are, usually, lower. The increase in toxic aluminium forms is mainly due to the increase in the concentration of $Al(OH)_4^-$ linked to an increase in pH (Fig. 2).

The upstream catchment of the river Vienne is very rich in macrophytes. During summer, due to high photosynthetic production and consumption of CO_2, the pH of the water increases from its usual level around 6.5–7.0 to 8.0, and aluminium solubility ($Al(OH)_4^-$ form becomes predominant) can increase if we refer to the work of Gislason et al. [16] carried out on Lake Ellidaar (Reykjavik, Iceland). Nevertheless, the results found in literature about the real toxicity of $Al(OH)_4^-$ for fish are conflicting. For Gundersen et al. [17], $Al(OH)_4^-$ is highly toxic for Atlantic salmon at a low concentration (20 $\mu g\ L^{-1}$) but in contrast for Poleo et al., [18], the toxicity of the $Al(OH)_4{}^-$ form is not clearly identified.

6. Conclusion

Organic matter and phosphorous play an important role in aluminium speciation. In a previous study [12] no evidence was found for aluminium concentrations that are potentially harmful to fish in upstream catchments of the river Vienne, but an extended dataset is now indicating that they are, if we consider the toxic forms of aluminium as being the sum of the Al^{3+}, $Al(OH)^{2+}$, $Al(OH)_2^+$ and $Al(OH)_4^-$ concentrations. Clearly there is need for long term and probably more intensive measurements to check the extreme cases when biota may be affected. On the river Vienne upstream catchment, the computation of aluminium speciation shows that toxic concentrations of inorganic aluminium appear during summertime, mainly due to the increase in the concentration of $Al(OH)_4^-$, produced by an increase in pH above 7.

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