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Role of natural organic matter in the mobility of aluminium ions in rivers in the Limousin region (France)

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Abstract – In order to investigate, in the Limousin (France), the role of organic matter in aluminium mobility in soil towards rivers and its chemistry in water, three different A₁ horizons of an acidic brown-earth soil planted with three different types of trees (chestnuts (*Castanea sativa*) over 100 years old, young Douglas fir (*Pseudotsuga menzesii*), and old Douglas fir) were selected, as well as five points on major rivers (Vienne, Vézère, Gartempe, Grande Creuse) in the area. The aluminium content of the rivers in the Limousin was evaluated. Characterisation of horizons, speciation of aluminium, and laboratory experiments on aluminium release from soil columns pointed out the probable origin of aluminium in the rivers and the role of organic matter in its mobility. This study showed that many rivers exhibit aluminium concentrations higher than 110 ppb, very low mineralization and an acid pH. The high concentration in aluminium may be due to the presence of coniferous forests on the river catchment. In an area preserved from human activity, the natural organic matter prevents aluminium precipitation despite the pH conditions (close to 5.5–6) which favour insoluble forms. On the contrary, when some physico-chemical conditions of the river change (increase in pH and supply of organic matter due to slight human or agricultural pollution) the aluminium may be removed, probably by precipitation with the organic matter.

aluminium / water quality / organic matter / forest

Résumé – Rôle de la matière organique naturelle dans la mobilité de l'aluminium dans les cours d'eau en Limousin (France). Pour étudier le rôle de la matière organique, en Limousin (France), sur la mobilité de l'aluminium des sols vers les cours d'eau et sa chimie dans l'eau, les trois horizons A₁ d'un sol brun acide planté de trois forêts différentes (châtaigniers (*Castanea sativa*), jeunes Douglas (*Pseudotsuga menzesii*), Douglas centenaires) et cinq points sur quatre des principales rivières (Vienne, Vézère, Gartempe, Grande Creuse) de la région ont été sélectionnés. L'état de contamination par l'aluminium de plusieurs rivières de la région Limousin est étudié. L'origine probable de l'aluminium dans les cours d'eau et le rôle de la matière organique dans la mobilité de l'aluminium sont montrés et étudiés à partir de la caractérisation des sols, de la spéciation de l'aluminium, et d'expériences de laboratoire réalisées principalement en colonne de sols. Certaines rivières présentent une concentration en aluminium supérieure à 110 ppb, une très faible

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minéralisation et un pH acide. La forte concentration en aluminium est probablement due à la présence de nombreuses surfaces boisées en conifères sur le bassin versant. Dans les zones préservées des pollutions domestiques ou agricoles, la matière organique présente empêche la précipitation et la disparition de l'aluminium malgré des pH défavorables aux formes solubles. À l'opposé, quand les conditions physico-chimiques des eaux changent sous l'effet d'une pollution domestique ou agricole diffuse (apport de matière organique, augmentation du pH) l'aluminium peut disparaître, probablement par des phénomènes de coagulation floculation.

aluminium / qualité des eaux / matière organique / forêt

1. Introduction

Soil organic matter which results from the biological and chemical decomposition of litter plays a major role in the mobility of the aluminium ion in soil and toward rivers [11]. Aluminium in the soil is present in different forms: adsorbed onto particles, complexed with organic matter or anions, precipitated as nodules, integrated into the crystalline structure of clays [11]. Some complexing sites on natural organic matter have been evidenced, notably for soil fulvic acids: sites analogous to that of salicylic acid (very widespread) and phenolic sites (widespread but rarer) [12]. In soil, the complex formed between aluminium and fulvic acids are chemically stable [19]. In stream water, aluminium bound to organic matter may stay in solution even if the pH conditions should lead to its precipitation [28], but it is the physico-chemical conditions of rivers that control the forms and the concentration of aluminium in water. For example, in a very acid river highly polluted by aluminium, soluble aluminium precipitates when the pH becomes less acidic ($\text{pH} > 5.5\text{--}6$). As a consequence, precipitates of amorphous aluminium can be found in river sediment [20].

The high concentrations of aluminium in soil or in stream water due to coniferous cultivation on poor soil and/or acid rain [10, 30] may lead to toxic effects on trees [4] or on aquatic life [18].

In France several studies have shown in the Vosges and/or Ardennes [8, 21, 23, 24] the impact of acid rain and intensive forestry on soil and stream acidification. Several streams in the Vosges show very acidic pHs and a high concentration of

aluminium. Thomas et al. [27] have shown the influence of soil, geology and relief on stream acidity in the Vosges. They have shown that at base flow, stream water acidity depends primarily on the bedrock and the soil content of weatherable minerals that neutralize acidity. As a consequence, much damage may be caused to aquatic life. The Limousin presents some characteristics similar to the Vosges: "poor" soil on a granite platform, acid streams with low mineralization and a high density of resinous trees which is increasing every year ($18 \text{ km}^2 \cdot \text{y}^{-1}$ for Limousin [9]). In the Limousin, Douglas culture leads to soil modifications such as acidification, increase in organic matter concentration and aluminium mobility [13, 14]. Douglas fir cultures lead to less acidification than other species of conifer such as Norway spruce [3].

Up to now, in the Limousin, no studies have been carried out on the aluminium content of streams and the behaviour of this element in water. The aim of this study is to investigate the state of contamination by aluminium of some Limousin rivers, the behaviour and fate of aluminium in water are also examined, in order to show the role of organic matter in its mobility from soil towards streams and in its behaviour in stream water.

2. Materials and methods

2.1. Aluminium in the rivers

2.1.1. Characteristics of the river sections studied

Table I gives some characteristics of the river waters which were chosen for this study.

Table I. Location and characteristics of the studied rivers.

River Location	Vienne Peyrelevade	Vienne Royère	Vézère Bugeat	Grande Creuse Clairavaux	Gartempe Maisonnisses
Altitude (m)	805	260	702	665	562
Geology	Granite at 2 micas	Granites	Granite with biotites or with 2 micas	Anatexites with cordierite Granites	Granite with biotites
Vegetation	Forest Moor Peat bog	End of woody area – Grassland	Forest Moor Peat bog	Forest	Forest Moor
km from spring	4	89	24	4.5	4
Size of catchment (km ²)	22	1150	75	12	35
Annual average flow m ³ ·s ⁻¹	1.8	25.2	4.5	1.2	0.18
Quality *	1 A Very Good	2/1B Passable-Good	1A Very Good	1A/1B Good	1A/1B Good

* According to French Water Agency criterions.

These streams cross the same kind of area: granite platform and highly wooded area with a high density of conifers. Their water qualities are very good or good according to French Water Agency criteria.

Two points on the Vienne river, Royère and Peyrelevade (higher up than Royère and about 85 km away), were chosen in order to examine the effects of the changes of the physico-chemical parameters of the river on the chemistry of aluminium in water.

2.1.2. Sampling

The river samples were collected during the period of May 1998 to January 2000 (or March 2000 for total aluminium). At the end of each month, some or all the points were sampled. Before analysis, the samples were stored at 4 °C in a Nalgene bottle, always for less than two days.

2.2. Aluminium in the soils

2.2.1. The soils

Brown acidic soils, which are very widespread in the Limousin (France) were used. The soils were

sampled in September 1993, 20 km to the south of Limoges (Lambert II coordinates: 365, 5078), on the Briance river catchment. They were taken from the same geological platform (gneiss) and area but planted with different species: Chestnut (*Castanea sativa*) (over 100 years old), young Douglas fir (*Pseudotsuga menziesii*) (about 15 years old) and old Douglas fir (100 years). The A₁ horizons were chosen because they might contaminate the subsurface water and to a lesser extent the run-off water (in so far as the soil litter is shallow) which supplies water to the stream.

For each soil, the A₁ horizons were taken, then differentiated according to structure and colour, after removal of litter. Each batch of soil horizon was made by mixing 10 samples taken from a 100 × 100 m square. The depth of the A₁ horizons were 12 cm for chestnut soil, 2 cm for young Douglas, and 5 cm for old Douglas. The soils were left to dry for two weeks at 20 ± 2 °C and sieved through a 2 mm mesh. They were stored in plastic bags in the dark.

2.2.2. Soil analyses and aluminium speciation

The organic matter content and pH_{H2O} of the soils were carried out under AFNOR French norms [2],

respectively AFNOR X31-109 and AFNOR X31-103. The evolution of the numerous pedological characteristics was the object of a previous study [14, 15].

The speciation of aluminium in the different A_i horizons of the soils was carried out using a parallel rather than a sequentially based protocol according to Jeanroy [17] and Ranger et al. [25]. The following fractions of aluminium could be distinguished: extracted with KCl, with pyrophosphate, with oxalic buffer pH and with tricitrate, bicarbonate and dithionite. These fractions might correspond respectively to aluminium that is easily exchangeable, bound to organic matter, amorphous and badly-crystallised.

In order to compare the different horizons with each other the extracted fractions are presented relative to the total aluminium present in the horizon studied. The total aluminium content of each horizon was assayed by the central analysis service of the CNRS at Vernaison. The aluminium in the extracts obtained was measured by ICP-MS by the same service.

2.2.3. Experiments on the released aluminium ions in a batch reactor and soil column

All these experiments were carried out in distilled water to show the role of organic matter in the soil on the release of aluminium by it. No salts were added to set ionic strength because cations may have provoked aluminium release by an exchange reaction [16].

For kinetics experiments in the batch reactor, five grams of C horizon of old Douglas soil were placed in a 180 ml flask to which was added 100 ml of solution (distilled water equilibrated with the atmosphere at pH 5.5 or a solution of humic substances).

The Commercial humic substances (Aldrich, (AHc)) were dissolved in distilled water at an initial concentration of $100 \text{ mg} \cdot \text{L}^{-1}$, shaken for 4 h then filtered through a $0.45 \mu\text{m}$ filter.

The flasks were placed on an orbital shaker whose speed was set at 100 movements per minute. During the study of the kinetics of dissolution, shaking time varied from 15 minutes to 24 hours.

For experiments in the soil column, a glass column was filled with 15 g of soil, according to Guibaud and Ayele [14]. Distilled water was percolated through the column and soil solutions were collected as a function of time.

2.3. Sampling treatment

2.3.1. Soil solutions

All soil solutions obtained from batch or column experiments were treated in the same manner:

- low pressure filtration using a $0.3 \mu\text{m}$ nitro-cellulose Sartorius membrane (for batch experiments this step was preceded by centrifugation for 15 minutes at 8000 revolutions per minute (5600 g));
- measurement of filtrate pH, dissolved organic matter (absorbency at 254 nm) and monomeric aluminium.

2.3.2. Stream samples

All stream samples collected were first treated by a low-pressure filtration using a $0.45 \mu\text{m}$ nitro-cellulose Sartorius membrane, followed by: measurement of filtrate pH; conductivity at 25°C ; dissolved organic carbon (DOC) (Dorhman Phoenix 8000 analyser); monomeric aluminium; total aluminium (Zeeman correction graphite furnace ASS 800 from Varian); Ca^{2+} , Mg^{2+} , SO_4^{2-} , NO_3^- (DX-100 Ionic Chromatography from Dionex); NH_4^+ , NO_2^- , PO_4^{3-} (colorimetric method of French AFNOR Standard for Water [1]).

2.3.3. Monomeric aluminium ion measurement

The Chromazurol S [22] colorimetric method was chosen to estimate free or weakly bound aluminium concentrations, as it allows us to quantify specifically the monomeric forms of aluminium. This method is based on the formation of a coloured complex between Chromazurol S and the aluminium ion, whose assay is performed at $\lambda = 567.5 \text{ nm}$ in an environment buffered to pH 4.6 using a buffer made from sodium acetate and acetic acid. A Shimadzu UV-visible apparatus was used to read the absorbency of the solutions. This method can be used to assay the aluminium monomer in aqueous

Table II. Minima and maximal values of different parameters recorded since May 1998 to January 2000 (¹or March 2000).

River Location	Vienne Peyrelevade	Vienne Royère	Vézère Bugeat	Grande Creuse Clairavaux	Gartempe Maisonnisses
pH	5.7–6.3	6.5–7.1	5.6–6.4	6.7–7.2	6.5–6.9
Conductivity ($\mu\text{S}\cdot\text{cm}^{-1}$)	21–27	37–61	17–24	43–68	44–76
Dissolved Organic Carbon (ppm C)	2.7–8.4	3.0–7.1	2.9–10.2	2.0–3.9	6.0–12.2
Total aluminium (ppb) ¹	33–118	20–72	45–145	19–56	79–163
Monomer aluminium (ppb)	11–79	0–30	13–41	3–33	22–51
Other ions ($\text{mg}\cdot\text{L}^{-1}$)					
Alkalinity (in HCO_3^-)	5–7	9–17	4–6	10–18	10–23
Ca^{2+}	1.1–1.6	2.4–3.9	1.0–1.7	2.5–4.6	2.9–5.1
Mg^{2+}	0.4–0.6	0.9–1.5	0.2–0.6	1.0–1.7	0.9–1.5
SO_4^{2-}	0.4–1.6	2.0–2.6	0.8–1.7	2.0–5.2	2.2–6.2
NO_3^-	1.3–2.1	3.0–6.0	1.0–2.9	3.0–6.8	1.4–3.6
NO_2^-	<0.01	0.01–0.07	<0.01–0.03	<0.01–0.04	0.01–0.05
NH_4^+	<0.02	0.01–0.07	<0.02	0.01–0.03	0.01–0.03
PO_4^{3-}	<0.03–0.18	<0.03–0.12	<0.03–0.15	0.03–0.44	0.03–0.43

solutions that have been in contact with soil, under the condition that ascorbic acid is added to eliminate any interference, notably with Fe^{3+} ions [14].

3. Results

3.1. Stream water quality

Table II presents the results obtained for the period May 1998 to January 2000 for some physico-chemical parameters. Only minimal and maximal values obtained are shown.

Figure 1 presents the evolution of aluminium concentration in stream water (Gartempe, Vienne at Royère, Grande Creuse) as a function of time. The other two rivers present a similar evolution.

Low NO_3^- and phosphorus (PO_4^{3-}) concentrations suggest no agricultural and/or human pollution at Vézère and Peyrelevade (Vienne). For these two rivers, base cation concentration, alkalinity, and

the mineralization (estimated by conductivity) were very low and the pH was acidic (Tab. II).

For the three other points the pH was weakly acidic or close to neutral and conductivity higher than for the Vézère and the Vienne (Peyrelevade). This was due to agricultural and/or human impact.

The pH variation was greater for the rivers with low conductivity. The buffer capacity of the Vézère and the Vienne at Peyrelevade was weaker than the three other samples, due to the ionic composition (Alkalinity, Ca^{2+} , Mg^{2+} ; Tab. II).

Aluminium levels were higher than 100 ppb in the Vienne (Peyrelevade), Vézère (Bugeat), and Gartempe (Maisonnisses). Moreover, for the affected rivers, the pH was acidic and the mineralization (estimated by the conductivity) was low or very low. Under these conditions, the concentration of monomeric aluminium seems to increase (Tab. II).

As shown in Figure 1, the evolution of the concentration of aluminium in stream water seems cyclic. The low aluminium contents were obtained

Figure 1. Example (Gartempe – Vienne at Royère – Grande Creuse) of evolution total aluminium content of the water as a function of time.

during the summer period. The large increase in aluminium concentration in summer, corresponded to a period of rainfall before the sampling time. A higher concentration can be observed in winter.

The Royère point is lower down than the Peyrelevade one (about 85 km away). The samples from the two points on the Vienne were taken on the same day, so the river was in the same hydrological state. At these two points, the geological characteristics are similar (Tab. I), but there is some agriculture and municipal sewage discharge between the two. The physico-chemical parameters of rivers are thus affected by this: there are increases in the pH (close to neutral), conductivity and nitrogen (NO_3^- , NO_2^- , NH_4^+), and phosphorus levels. Many physico-chemical parameters such as pH or conductivity may be influenced naturally by the increase in the catchment surface area. Despite crossing a woody area, which could increase the concentration in aluminium or decrease pH, the concentrations of aluminium recorded at Royère were lower, and the pH was higher than those of Peyrelevade.

3.2. Relation between physico-chemicals parameters of the water

3.2.1. pH – Dissolved Organic Carbon

Figure 2 presents the correlation obtained between pH and the concentration of dissolved organic carbon.

For each river, the pH decreases linearly with an increase in concentration of organic matter. Two groups of river can be distinguished: Vézère - Vienne (Peyrelevade) and Vienne (Royère) - Gartempe - Grande Creuse.

The division into two groups seems to be related to river mineralization (estimated by conductivity, Tab. II) which leads to the consideration of the buffer capacity of the rivers. For the rivers with very low mineralization, the coefficient of determination obtained ($r^2 = 0.73$ Vézère; $r^2 = 0.83$ Vienne Peyrelevade) shows that the concentration of organic matter may play a major role in the regulation of river pH. For the other group of rivers with a higher mineralization (and so a buffer capacity), the dispersion of results around the draw line ($0.32 < r^2 < 0.45$) suggests that it is not only the organic matter

Figure 2. Relation between pH and dissolved organic carbon (DOC, in ppm of carbon) of the different rivers.

that determines river pH. Ions, such as hydrogenocarbonate, calcium, and magnesium (Tab. II) in higher concentrations than for the first group of rivers may also influence pH regulation.

3.2.2 pH – Aluminium

Figure 3 shows the correlation obtained between pH and concentration of total or monomeric aluminium for the Vienne (Royère) and Vézère rivers. The same results are obtained for both. The evolution between pH and Aluminium observed for Gartempe and Grande Creuse is identical to the Vienne (Royère) ones.

For the Vézère and Vienne (Peyrelevade), total and monomeric aluminium concentration decreases linearly (r^2 respectively 0.52 and 0.73 for total aluminium; r^2 respectively 0.78 and 0.58 for monomer aluminium) with an increase in pH. The aluminium precipitates when the pH increases and then disappears from the water, in accordance with Clavery et al.'s results [7].

No such direct effects have been observed for the other rivers.

3.2.3 Dissolved Organic Carbon - Aluminium

Figure 4 can be used to correlate the concentration in dissolved organic carbon and the concentration of aluminium.

Figure 3. Relation between pH and total or monomer aluminium for Vézère (a) and Vienne at Royère (b) rivers.

Figure 4. Relation between dissolved organic carbon (DOC, ppm C of carbon) and total or monomer aluminium for Vézère (a) and Vienne at Royère (b) rivers.

For the rivers with very low conductivity (weakly buffered water), the Vézère and the Vienne (Peyrelevade), total (r^2 respectively 0.47 and 0.59) and monomeric aluminium (r^2 respectively 0.42 and 0.77) concentrations increase with the amount of dissolved organic carbon.

The development for total aluminium as a function of the level of organic matter obtained for the other group of rivers is the reverse of that obtained for the Vézère and Vienne (Peyrelevade). The concentrations of total aluminium decrease with dissolved organic carbon concentration (r^2 values: Vienne at Royère 0.25; Grande Creuse 0.48; Gartempe 0.54). The amount of monomeric aluminium increases with organic matter concentration (r^2 values: Vienne at Royère 0.65; Grande Creuse 0.55; Gartempe 0.88).

3.2.4. Relation between aluminium concentrations and conductivity

In order to confirm aluminium chemistry and the role of organic matter in its mobility, other correlations can be carried out. Figure 5 presents the relation between total aluminium and conductivity.

The concentrations in total aluminium progress in a linear way as a function of conductivity, but

there are two kinds of evolution. The Vézère and Vienne (Peyrelevade) rivers, which have very low mineralization, exhibit an increase in the concentration of total aluminium with conductivity. For the Gartempe, Grande Creuse and Vienne (Royère) rivers, the total aluminium concentration decreases with conductivity.

3.3. Effect of organic matter on aluminium mobility in soil

In order to explain the origin of aluminium in stream water some soil characteristics of the Limousin area were collected and studied. Moreover the role of organic matter in aluminium mobility was investigated in A_1 horizon of soil.

3.3.1. Characteristics of A_1 of horizons of chestnut and Douglas fir soils

Figure 6 presents the organic matter content (Fig. 6a) and pH (Fig. 6b) of the water of the three A_1 horizons from Douglas fir and chestnuts soils.

The A_1 horizons of Douglas soil had an organic matter content higher than that of the chestnut (Fig. 6a). The amount of organic matter increases

Figure 5. Relation between conductivity (25 °C) and concentration of total aluminium of the different rivers.

with the age of the plantation for Douglas soils. This may be due to the difference in A₁ horizon thickness and/or cultivated species and its age. Soil pH decreases as the amount of organic matter increases (Fig. 6b).

Figure 7 presents the aluminium speciation in A₁ horizons: chestnut, young Douglas, and old Douglas.

The quantity of all aluminium fractions increase for A horizon of Douglas soil. For our soil, the concentration of the most mobile fraction – KCl and pyrophosphate extracted aluminium (may be bound to organic matter) – increases greatly with the age of the Douglas plantation. This is due to the increase in the amount of organic matter in the soil and to acidification.

Figure 6. Effect of Douglas culture on the concentration of Organic Carbon (a) and pH_{H₂O} (b) on to A horizon of a Limousin acidic earth brown soil.

Figure 7. Aluminium speciation in A_1 horizon of a limousin acid earth brown soil planted with 3 different forests.

3.3.2. Soil column experiments

Figure 8 shows the correlation between the concentration of aluminium and the estimated organic matter released by the three A_1 horizons, in the soil column experiments.

The correlation obtained was very good. In soil, the aluminium seems to migrate with the organic matter. This suggests that the solubilization of organic matter in the soil involves a weathering of soil or the release of aluminium bound to organic matter.

3.3.3. Effect of the addition of organic matter on aluminium release

The C horizon of the old Douglas soil which contains little organic matter (0.2% in organic carbon),

was mixed with a solution of commercial Aldrich soil humic substances ($100 \text{ mg} \cdot \text{L}^{-1}$) to test the latter assumption. The results obtained are presented in Figure 9.

In distilled water, the soil can not release aluminium as there is no cation to exchange with it (according to Guibaud and Ayele [16]) and the amount of organic matter was far too low to have involved weathering of soil particles over the 20 hours of the experiments. Aluminium release occurred in the presence of Aldrich soil humic substances. At first, release occurred rapidly, which may have been due to desorption of aluminium due to the complexing capacity of AHc. In a second step, the rate of aluminium release greatly decreased. The release equilibrium was not reached after

Figure 8. Correlation between aluminium and organic matter (measured by absorbance at 254 nm) released by each A horizon studied in soil columns.

Figure 9. Effect of Humic substances (AHc) on aluminium release by C horizon of old Douglas soil.

20 hours of contact. The presence of humic substances may provoke weathering of the soil, due to the complexing proprieties of humic substance for metal ions. Stumm and Furrer [26] studied the effect of organic compounds (models of natural organic matter) on the solubilization of the synthetic mineral: $\delta\text{-Al}_2\text{O}_3$. No equilibrium state could be reached over the period of time spent on the kinetics experiments. They concluded that the organic compounds induced a solubilization of aluminium from the mineral. Our kinetic results agree with those of Stumm and Furrer [26].

4. Discussion

Some rivers in the Limousin have elevated aluminium concentrations. In Norwegian rivers, the pollution limit concentration for aluminium is 110 ppb as given by Christophersen et al. [6]. Moreover, in their case, the concentration of aluminium released by soil and measured in neighbouring rivers was enhanced by acid deposition. These authors consider a natural concentration of aluminium as being inferior to 30 ppb. They (Christophersen et al. [6]) showed that rivers with a catchment area exhibiting a very high density of conifers and no great acid deposition, may reach aluminium concentrations of about 210 ppb. There is very low acid deposition in Limousin [29] but on the other hand the area planted with coniferous trees on river catchments is increasing all the time.

Therefore, we can suppose that the origin of the elevated aluminium content in these streams may be a result, to some extent, of the development of coniferous cultivation.

The low pH combined with the concentration in aluminium may cause damage to aquatic life. Probst et al. [23] lay down the pH limit and aluminium concentration for the disappearance of trout in Vosges streams at 5.6 and 170–180 ppb, respectively. Such values are close to being reached in the Vienne (Peyrelevalde) and Vézère rivers.

The evolution of aluminium concentration in stream water as a function of time may confirm the source of the type of the water supplied to the rivers, according to Dambrine et al. [8]. In summer, during the dry period, rivers seem to be supplied with water which comes from a deep layer of soil, which may neutralise aluminium. During a period of heavy rainfall (in summer or in winter), streams seem to be supplied by run off water or subsurface water. The aluminium is not precipitated in the soil and can reach the river.

In a river, the concentrations of aluminium depend on its physico-chemical characteristics such as pH and organic matter. Lukewille and Van Breemen [20] investigated the aluminium concentration in a river. Upstream, they measured a high concentration of aluminium and acid pH. Below this area, the quality of water was modified and the pH became alkaline. In fact, the aluminium concentration decreased greatly. Amorphous aluminium precipitates could be observed in river sediments. These results point out the importance of the physico-chemical characteristics in the behaviour of aluminium in a river. In order to obtain information concerning these properties some correlation can be established between the physico-chemical parameters of water. The greater the buffer capacity of a river is, the less the supply of organic matter influences the river pH. For a river with a low buffer capacity, the aluminium may precipitate with an increase in pH. When the buffer capacity increases, there is no relation between pH and aluminium in solution. This may be due to the low variation in pH close to neutral, and in the region at which aluminium precipitates. The forms of aluminium present in

water may be aluminium bound with organic matter, polymeric aluminium or amorphous aluminium, according to the study of Boudot et al. [5].

For the Vézère and Vienne at Peyrelevade, aluminium content of the water increased with the dissolved organic matter. The presence of an aluminium-organic matter complex may prevent the precipitation of aluminium, even if the pH conditions are unfavourable for the soluble form of aluminium. These results are in accordance with Tipping et al. [28]. For a pH of about 6, the aluminium-organic matter complex does not precipitate despite unfavourable pH conditions for aluminium in the soluble form. In this kind of river, the subsurface and run-off water from neighbouring forests may carry aluminium bound with organic matter. The third part of this study shows the role of organic matter in the mobility of aluminium in soil and may explain the presence of aluminium in stream water when they pass through densely wooded areas.

The Vienne at Royère, Grande Creuse and Gartempe showed a decrease in aluminium with an increase in organic matter. The following assumption may be made to explain these results. These rivers have a pH close to neutral, at this pH the aluminium precipitates easily. It seems that aluminium and organic matter co-precipitate together by coagulation-flocculation mechanisms. This hypothesis may be confirmed by the results presented in Figure 1, which show the pH to be higher the lower the concentration of organic matter.

The evolution of aluminium content as a function of conductivity may confirm the origin of the aluminium and the effect of human impact on it. For the Vézère and Vienne at Peyrelevade, there is no human impact and the low conductivity has a natural origin. The level of conductivity and the aluminium concentration may originate from the weathering of the soil surface by protons and organic matter. As a consequence, ions, organic matter, protons and aluminium may be present in subsurface and run off water, and can contaminate streams. For the three other points sampled, part of the conductivity came from human pollution (agriculture or municipal sewage), which is in accordance with the values of Table II. These kinds of pollution are a

source of organic matter or alkalinity. As a result, there is modification of the physico-chemical parameters of the river and a decrease in aluminium concentration.

5. Conclusion

This study shows that some rivers in the Limousin exhibit high concentrations of aluminium, which may be due to the development of coniferous cultivation. But even rivers preserved from human or agricultural impact exhibit aluminium pollution. Low mineralization and the acid pH may enhance the toxic effect of aluminium on aquatic life. When the physico-chemistry is affected by human pollution, aluminium may be precipitated when there is an increase in pH and/or with the presence of organic matter. In this case, the concentration of aluminium decreases in the river, but aluminium pollution still exists potentially.

This study has pointed out that organic matter plays a major role in the migration of aluminium from soil toward streams as well as in its chemistry in water. In river water, when the pH is acidic (about 5.5–6) the organic matter prevents aluminium precipitation. On the contrary, when the water pH is close to neutral, the organic matter seems to provoke the precipitation of aluminium perhaps by a coagulation-flocculation phenomenon.

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