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Soluble and colloidal translocation of Al, Fe, Si and Mn in an artificially drained French Retisol

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Abstract

Soil evolution results from both solute and colloid/particle translocation, but their relative importance in terms of soil formation is still under debate. The genesis of albic material in Retisols represents an ideal case to quantify the relative contribution of these two forms of transport in soil evolution since it results from i) clay eluviation, ii) reductive solubilisation of Fe oxides, and possibly iii) silicate hydrolysis. This issue seems particularly challenging in cultivated Retisols in which detailed analysis of the soil solid phases has demonstrated that

artificial drainage and liming alter the genetic pathway of albic material both qualitatively and quantitatively.

In the present study, we characterised the chemistry (pH, Eh, Al, Si, Fe and Mn) and dynamics of soil water and its evolution with increasing distance from the drain. Rainfall water, soil solution at water saturation in the E&Bt horizon and drainage water were sampled by an open rainfall collector, piezometers located at different distances from the drain, and an automatic water collector located at the main drain outlet, respectively.

An element budget at the profile level revealed that only Si was lost from the soil profile while the leaching losses of Al, Fe and Mn were overcompensated by deposition from the atmosphere. The constant Fe/Al concentration ratios in piezometers and drain waters as well as the breakthrough curves at the drain outlet for individual rainfall events suggested that Fe and Al were exported together and mainly in colloidal form. While this was also partly true for Si, a longer tailing of the Si than the Fe and Al breakthrough curves indicated that Si was additionally transported in soluble form. Lastly, the temporal variation of the Mn concentrations was unrelated to that of the other elements, pointing to the predominance of translocation in soluble form. All these results demonstrated that: i) particle/colloidal translocation is more important than translocation in soluble form in a drained Retisol; ii) reductive solubilisation of Fe and Mn oxides still occurred, in spite of the artificial drainage; iii) processes such as wet and dry deposition, dissolution of quartz or ferrollysis also contribute to element budgets in Retisols, at least at some microsites and in some years.

Key-words

Clay translocation; translocation in soluble form; reducing conditions; ferrollysis; soil water monitoring; pedogenesis

Highlights

Clay translocation is the main pedological driver in an artificially drained Retisol

Extremely wet years play a key role in soil evolution on decade scale

The hierarchy of soil processes changes in time with environmental conditions

Reducing conditions are restricted in both time and space

1. Introduction

Soil evolution results from both solute and colloid/particle translocation, but their relative importance in terms of soil formation depends on the soil type (Bockheim and Gennadiyev, 2000). In Ferralsols or Podzols, for instance, translocation in soluble form is largely dominant (Irion, 1984; Lucas et al., 1986; Chauvel et al., 1987; Boulet et al., 1997; Lundström et al., 2000). Bern et al. (2015) showed through a laboratory and modelling approach along a South Africa soil toposequence developed on granite and gneiss under a semi-arid, monsoon climate that colloid translocation, which has generally been neglected, is quantitatively important. In another pedological context, the development of soil (Luvisols) was described as a result of both particle physical weathering and particle translocation (Jamagne, 1978; Jamagne and Pedro, 1981; Hardy et al., 1999; Bockheim and Gennadiyev, 2000). Recent work, however, has questioned the quantitative importance of translocation in the formation of Luvisols (Legros, 2007; Quénard et al., 2011). Goddérís et al. (2006) and Finke and Hutson (2008) claimed to be able to model Luvisol formation based on a model focusing respectively on chemical weathering and on physical weathering plus particle translocation, demonstrating the interlocking between particle and solute translocation to describe the formation of the Bt horizon. More recently Keyvanshokouhi et al. (2016) concluded that chemical weathering and clay precipitation also probably take place besides particle physical weathering and translocation in the formation of the lutum accumulation in the Bt horizon of the Luvisols developed on loess. Lawrence et al. (2015) showed that the Bt horizon corresponds to the secondary mineral precipitation zone. All these previous studies demonstrate that there is a need to better quantify the relative importance of these two kinds of matter transport in the field.

The genesis of albic material in Retisols (IUSS working group WRB, 2014; previously called Albeluvisols, IUSS working group WRB, 2006) was chosen as a model case to study the relative importance of solute versus particle translocation for the following reasons.

First, the relative importance of a “soluble” and a mixed “soluble/particulate” pathway has long been debated in the literature on the genesis of albic material in this soil type (Van Ranst and De Coninck 2002; Szymanski et al., 2011; Szymanski et al., 2017). The first pathway called ferrollysis involves the destruction of clay mineral lattices by acid hydrolysis (Brinkman, 1970, 1977, 1979; Barbiero et al., 2010), while the second pathway consists of the dispersion and translocation of clay after reductive removal of Fe oxides bridging clay particles (Jamagne, 1978; Pédro et al., 1978; Payton, 1993; Van Ranst and De Coninck, 2002; Weisenborn and Schaetzl, 2005).

Second, while a general agreement on the mixed pathway is emerging for acid and poorly drained Retisols (Jamagne, 1978; Pédro et al., 1978; Payton, 1993; Van Ranst and De Coninck, 2002; Weisenborn and Schaetzl, 2005), Montagne et al. (2013, 2016) described the development of albic material induced by agricultural drainage in a cultivated Retisol despite high soil pH values due to liming. On the basis of a detailed analysis of the soil solid phases, Montagne et al. (2013, 2016) suggested that in such a limed and drained Retisol, the genesis of albic material was mainly driven by $< 2 \mu\text{m}$ particle translocation without significant implication of translocation in soluble form. For these reasons, we considered with Bockheim and Hartemink (2013) that the incidence and relative intensity of the “soluble” and the “particulate” pathways still need to be clarified, particularly in cultivated Retisols.

In this study, we monitored during a three-year period the chemistry of the soil water along a soil drainage sequence, extensively studied by Montagne et al. (2008, 2013, 2016) in order to:

- i) characterise the relative contribution of solute and particle translocation in the genesis of

albic material in a limed and drained Retisol; ii) clarify how reducing conditions are involved in the genesis of albic material after artificial drainage; and finally iii) determine the dynamics and the location of the different soil processes involved in the formation of albic material in cultivated and drained Retisol

2. Material and methods

2.1. Study site

The studied site consists of a 4-ha cultivated plot lying on the crest of the Yonne plateau, France, where Retisols developed in Quaternary non-calcareous loess deposited over an Eocene clay layer (Baize and Voilliot, 1988). The soil has been cultivated for at least 200 years (Cadastre, 1828) and was artificially drained in 1988 (16 years before soil sampling) by a subsurface drainage network located at 1 m depth in the Bt horizon. It comprises the 4 characteristic horizons of a cultivated Retisol developed in the loess deposit, namely: a silty, brown ploughed A horizon (0-25/30 cm); a silty grey E horizon (25/30-35/40 cm); and two horizons composed of a complex mixture of several soil volumes of distinctive colours. The most abundant soil volumes are silty and of a white-grey (10YR8/2 to 10YR7/1 moist) to pale-brown (10YR7/4 moist) colour in the upper horizon (35/40-55/60 cm), whereas they are clayey and of an ochre colour (10YR5/6 to 10YR5/8 moist) in the lower horizon (55/60-90/105 cm). Black concretions and impregnations occur in the core of the ochre volumes. For convenience, we call the upper horizon the E&Bt horizon hereafter, whilst the lower one is called the Bt horizon. Montagne et al. (2008, 2013, 2016), Frison et al. (2009) and Cornu et al. (2012a, b) extensively characterised the physical properties, the mineralogical and chemical composition, the abundance and morphology of the different soil volumes of the E&Bt and Bt horizons sampled along a 4-m trench dug perpendicularly to a drain on a flat area (Table 1). Montagne et al. (2008) showed that the relative abundance of the white-grey, pale-brown soil volumes and black concretions and impregnations increased in the E&Bt horizon for distances to the

drain less than 2 m. Conversely, the proportion of the clayey ochre soil volume decreased (Figure 1). No significant changes were observed more than 2 m away from the drain. This was interpreted as an increase both in the precipitation of Mn oxides and Mn-rich ferrihydrite and in the loss of $< 2 \mu\text{m}$ particles with decreasing distance to the drain due to a change in redox conditions and a higher eluviation intensity in the vicinity of the drain. Montagne et al. (2013) hypothesised that eluviation was mainly restricted to the first metre on each side of the drain line, whereas reducing conditions still occurred further on. Since the drain lines are spaced 15 apart, reducing condition still occurs on 13 m between two drain lines. The yearly total loss of lutum by eluviation via drainage was estimated to be 5 t ha^{-1} (Montagne et al., 2016).

2.2. Water sampling

Three types of water were sampled: the rainfall water as the input to the soil system, the soil solution at water saturation from the E&Bt horizon, and the drained soil water as the output from the soil system.

Rainfall water was collected by a 15-cm diameter funnel, placed about 1.5 m above the soil and connected to a 10-L-bottle by polyurethane tubing. A 0.5-mm nylon mesh was installed in the funnel to prevent leaves falling into the collector. This type of open rainfall collector samples wet atmospheric deposition as well as a part of the dry deposition.

Soil solution at water saturation in the E&Bt horizon was monitored and sampled by two piezometers located, down to the base of the E&Bt horizon, at each of three distances from the drain (70, 150 and 400 cm; Figure 1) in order to identify the potential impact of artificial drainage on soil water dynamics and chemistry. One piezometer was open, made of a PVC tube, and designed to measure the water level. The other one was dedicated to water sampling. It was made of Teflon and was closed to the atmosphere to avoid contact between the latter and

the soil solution. It was sampled by suction under vacuum. The piezometers were surrounded by a fine nylon mesh in order to minimize soil translocation to the piezometer.

Drainage water was sampled at the outlet of the main drain collecting waters from the 4-ha-plot. An automatic collector was located for that purpose at the main drain outlet.

Water sampling was performed during three and half years (January 2005 to June 2008), once a week during the first two years and once every two to three weeks during the remaining time.

The rainfall water sampling was initiated at the beginning of 2006. The soil was cropped with wheat in 2005, maize in 2006 and wheat followed by rape in 2007.

2.3. Water analysis

Soil water samples were analysed for Eh and pH directly in the field on unfiltered samples. For drained water, both pH and Eh were measured at the outlet of the drain on each field trip when water was running from it.

Eh was measured with a Pt electrode and a Ag–AgCl reference electrode. The measurements were then corrected to the standard H electrode by using a correction factor depending on the temperature (Kölling, 1999):

$$Eh_{\text{corrected}} = Eh_{\text{measured}} + [207 + 0.7(25-T)]$$

where T is the temperature (°C), and $Eh_{\text{corrected}}$ is the corrected redox potential (mV). As only corrected Eh values are presented hereafter, they are referred to as Eh for simplicity.

Back in the laboratory, electric conductivity was measured and the water samples were filtered at 0.2 µm on acetate filters. The filtration cut at 0.2 µm of the sampled water is classically used to remove the particles present in the water but this cut does not remove all colloids. Therefore elements present in the filtrate are not only present in soluble form but also in colloidal form (Pédrot et al., 2008). In the rest of this paper we will call particles the 0-2 µm soil fraction

previously analysed by Montagne et al. (2008, 2013, 2016), and colloids the solid fraction < 0.2 µm present in the water sample.

Water samples were then acidified with ultrapure HNO₃ and stored at 4°C before Fe, Mn, Si and Al analysis. For the 2005 and 2006 samples, Fe, Mn, Al, Si were measured by flame (Al, Fe) (Solaar AA Spectrometer GF 95, Thermo Elemental) and when under the limit of quantification by graphite furnace (Al, Mn) atomic absorption (Solaar AA Spectrometer GF 95, Thermo Elemental), and by colorimetry using the molybdate blue method for Si (Arozarena et al., 1989) and the orthophenanthroline method for Fe after reduction of the Fe³⁺ into Fe²⁺ by addition of hydroquinone. In 2007, the samples were analysed by ICP-AES (Ultima C, Jobin Yvon Horiba) for the 4 elements. For some water samples one aliquot was stored without acidification at 4°C for major anion and cation analysis. Major anions and cations were then analysed by ion chromatography (Dionex ICS 1000). The ionic strength (IS) was calculated with Eq. (1).

$$IS = \frac{1}{2} \sum C_i z_i^2 \quad (1)$$

where C_i represents the concentration of the anion/cation i and z_i its charge.

2.4. Monitoring of drainage and rainfall

An automatic bucket rainfall gauge collector was installed on the plot to measure rainfall. However as rainfall was not measured in 2005, for mass balance calculation purposes, Meteo France data from the SAFRAN grid were used (Quintana-Segui et al., 2008). Drained water discharge was continuously recorded by means of a V-notch weir (opening angle of 30 degrees) associated to a pressure sensor to measure the water level. The pressure sensor was calibrated and the ideal equation was then used to calculate the drainage volumes. Penman-Monteith

potential evapotranspiration (PET) provided by Meteo France (SAFRAN grid) was also used for mass balance calculation purposes.

2.5. Data processing: Mass balance calculation and statistics

Mass balance was computed by considering the effective rainfall (rainfall – PET) and the export occurring either at the base of the E&Bt horizon or at 1 meter depth, considered hereafter as the base of the soil profile. Rainfall water input was computed as the result of the rainfall provided by Meteo France and the Fe, Si, Al, and Mn concentrations measured on our samples. Export at the base of either the E&Bt horizon or of the soil profile was computed by taking into account the drainage discharge measured at the drain outlet and the concentrations in Fe, Si, Al and Mn measured respectively in the piezometer water and in the drainage water. The drainage discharge was used in both cases since it mainly drains the soil solution at water saturation of the A and E&Bt horizons, which are the only two horizons that are waterlogged during winter. Mass balance calculations were obtained according to Eq. (2).

$$\text{Gain/loss}_{X,E\&Bt \text{ or profile}} = ([X_{\text{rain}}] \times P - [X_{\text{piezo or drain}}] \times D) \quad (2)$$

where $\text{gain/loss}_{X,E\&Bt \text{ or profile}}$ represents the gain/loss in the element X at the base of the E&Bt horizon or of the soil profile respectively; $[X_{\text{rain}}]$, the concentration of the elements X in the effective rainfall; P, the effective amount of rain; $[X_{\text{piezo or drain}}]$, the concentration of the elements X in the piezometer or in the water collected at the outlet from the main drain respectively; and D, the water volume drained.

This mass balance calculation was performed over the three complete years (2005-2007). For this purpose, missing concentrations, for the rainfall notably, were estimated on the basis of average values \pm standard deviation after exclusion of the outliers.

Descriptive statistics of the main water characteristics (minimum, maximum, median, mean values and standard deviation) are reported in Table S1 (see supplementary data) for each of the three types of water considered, namely rainfall, piezometer and drain waters. To determine whether the piezometer waters with an Eh value higher and lower than 300 mV differed significantly in Fe, Mn, Al and Si concentrations, t-tests were performed at a 5% threshold level. Principal component analyses (PCA) were also carried out for the piezometer waters, considering the main water characteristics as variables, i.e. pH, Eh, Fe, Mn, Al and Si in order to identify a potential seasonal typology of the water samples.

3. Results

3.1. Temporal variation of rainfall: pluviometry and water chemistry

The sampled years were wetter than the average pluviometry of the region with 673 mm in 2005 and about 750 mm for the following two years against 645 mm on average (ten-year average, Meteo France data). While the monthly rainfall distribution was homogeneous throughout the year with monthly precipitation ranging from 42 to 63 mm on average (ten-year average, Meteo France data), the studied years exhibited dry months (with only 20 mm rainfall or less) and extremely wet months with more than 80 mm rainfall (Figure 2a). Rainfall chemistry was also highly variable in time with pH ranging from about 4.5 to 8 (Table S2 in the supplementary data). These pH values are in the range of the values gathered from the literature for rainfall in Central France (Négrel and Roy, 1998; Bertrand et al., 2008; Chetelat et al., 2009), with the exception of some extremely high pH values around 8 that were not recorded in those studies. The concentrations of Fe, Mn, Si and Al ranged from 0.2-1.4 $\mu\text{mol L}^{-1}$, 0.1-1.7 $\mu\text{mol L}^{-1}$, 0.3-21.8 $\mu\text{mol L}^{-1}$ and 0.2-3.1 $\mu\text{mol L}^{-1}$ respectively (Table S1), with peaks of Fe, Si, Al, Mn concentrations that were generally concomitant. These high concentrations were recorded in fall or early spring. Rainfall values of concentrations in Si, Fe, Al and Mn are scarce in the literature. The ranges found for Fe and Al are comparable to those provided by Cornu et al. (1998) for Amazonia, but the range for Si is larger. Négrel and Roy (1998) reported lower Al concentrations for the Massif Central (France). Since the rainfall collector was an open collector that also collects part of the dry deposition, we assumed that these high concentration peaks were due to soil dust when the soil surrounding plots was bare, notably during tillage periods.

3.2. Drain water chemistry over time

Drainage occurred (i) mainly from December to March, when the rainfall exceeded the PET (Figure 2b); (ii) as a succession of pulses periodically recorded during the drainage season (Figure S1A). The few small drainage events recorded in summer, corresponding to major storm events, were not sampled for chemical analysis. Drainage was not always proportional to the difference between rainfall and PET as it also depends on the history of the previous months, resulting in higher flow rates in the years 2005 and 2006 than in the years 2007 and 2008 (the highest being recorded in 2006).

The pH and Eh values were anti-correlated, with Eh values less than 300 mV recorded in 2005 and 2006 during the highest drainage period (Figure 3). This Eh value of 300 mV is considered as a threshold for anaerobic soils by Inglett et al. (2005). Al and Fe concentrations were positively correlated with an Al/Fe ratio close to 4 (Figure 4a). Cycles of peak concentrations followed by low concentrations were observed for these two elements (Figures 5a and b and detail on Figure S2), suggesting that their behaviour obeyed similar processes. These peaks often occurred more or less simultaneously with a peak of drainage (Figure 5 a and b). Mn concentration also showed peaks of concentrations (Figure 5c) that were not always in phase with those of Al and Fe (Figure S2). Si concentrations were almost two orders of magnitude higher than those of the other elements and were less variable in time (Figure 5d), with small oscillations and some larger peaks of concentrations concomitant with those in Fe and Al (Figure S2).

Compared to the rainfall water, concentrations in the drain were of the same order of magnitude for Fe and Al, but an order of magnitude higher for Si and smaller for Mn (Table S1; all the data for drainage water are reported in Tables S3 to S7 in the supplementary file).

3.3. Piezometer water chemistry in time and space

Soil water was available in piezometers whatever the distance to the drain from January to March in most years, and up to April at 400 cm from the drain. In 2007, water was also sampled at that distance in November and December (Table S9, supplementary file). This timing of the perched water tables is similar to those observed by McDaniel et al. (2001) or Rockefeller et al. (2004) in similar pedoclimatic conditions. When water was available in the piezometers, most of the E&Bt horizon was waterlogged, as well as the E and part of the A horizon in February 2005, March 2006 and spring 2008 (Figure S1b).

Concentrations in the piezometer were on average one order of magnitude higher for Fe, Mn and Al than average concentration of the drain water, but of the same order of magnitude for Si (Table S1). No clear difference in the chemical composition of the waters sampled by the piezometer was observed with distance from the drain (Figure S6). The principal component analysis (PCA) conducted on the chemical and physico-chemical characteristics of these soil waters explained 66 % of the variance with the first two factors representing 44% and 22 % of the variance (Figure S7) respectively. Factor 1 was defined by the opposition of Eh and pH, as classically observed in cases of reducing conditions and clearly visible in Figures 6 a and b. Fe and Al, like pH, were negatively correlated with Factor 1. In the sample space, this first factor defined two groups of samples. The first group consisted of waters collected in January and February 2005 and 2006 and at the beginning of March 2006. These waters were characterised by high Fe and Al concentrations, pH values > 8, and Eh values generally < 300 mV, the threshold value for anaerobic conditions (Inglett et al., 2005, Fig. 7). This first factor separated periods with reducing conditions from those with oxidizing conditions (second group formed by water collected after mid-March 2006).

Fe and Al concentrations in samples with Eh values < 300 mV were on average significantly higher than those of samples with Eh values > 300 mV, while Si concentrations were on average significantly lower for the same samples (Table 2). No differences were observed for

Mn. In addition, Al and Fe concentrations in waters having Eh values above 300 mV were linearly correlated with an Al/Fe ratio close to 4. For Eh values below 300 mV, concentrations in Fe increased more than those in Al (Figure 4b).

The second PCA factor opposed pH to Fe and Al, and was driven by two samples from January 2005, collected 70 cm from the drain and exhibiting particularly high concentrations in Fe and Al (Tables S8 and S9 in the supplementary file).

3.4. Gains and losses of elements at the scale of the E&Bt horizon and of the soil profile

Fe, Mn, Si and Al were exported through the drainage network each year (Table 3). The exports of Fe and Al showed a tendency to increase with the drainage discharge whereas export of Mn and Si was more constant through time (Table 3). The exports in Fe and Mn were however much lower than the atmospheric deposition for these elements. Thus part of the deposited Fe and Mn accumulated in the soil irrespective of the year (Table 3), mainly in the E&Bt horizon with the exception of 2005 for Fe. The fate of Al deposition was more variable in time: Al was accumulated in the E&Bt horizon in 2007, but only partly accumulated in the deeper soil horizons in 2005 and was exported from the soil in 2006 (Table 3).

A quantity of Si at least equivalent to that deposited was exported from the soil profile every year. Nevertheless, the deposition rates measured here were much higher than the rainfall inputs recorded in the literature (24 kg ha⁻¹ yr⁻¹ by Street-Perrott and Barker, 2008; less than 1.4 kg ha⁻¹ yr⁻¹ by Desplanques et al., 2006; less than 2 kg ha⁻¹ yr⁻¹ by Sommer et al., 2006), probably due to local input by dust as mentioned earlier, with export by the drain comparable to the export of Si from soils compiled by Sommer et al. (2006). Losses of Si from the E&Bt horizon were higher than those from the complete soil profile, irrespective of the year.

4. Discussion

4.1. Form of the elements present in the filtrated waters

The analysis of the element concentrations through time and for the different types of water should make it possible to differentiate between colloid translocation related to eluviation and translocation in soluble form resulting from mineral chemical weathering.

At the event scale, the concentrations in Al, Fe and Si increase with the drain discharge. The Al and Fe concentrations rapidly decline after individual event-caused peaks as typically observed for particle export (Grant et al., 1996; Kronvang et al., 1997; Laubel et al., 1999; Petersen et al., 2004; Montagne et al., 2009). That in Si remains high, ranging from 40 to 80 $\mu\text{mol L}^{-1}$ (Figure 5). Concomitant peaks of concentrations in Si, Fe and Al and the drain discharge thus seem to be linked to exportation in a colloidal form probably as fine or very fine clay minerals. Contrastingly, Si translocation during the recession part of the discharge curve may be associated with slow matrix flow (Kumar et al., 1997) and consequently be in soluble form (especially since only Si is highly exported then). The major export as colloidal form for Al and Fe but as soluble form for Si is also in line with the decrease in Al and Fe concentrations, but not in Si concentrations, from piezometer waters to drain waters (Table S1). Whereas colloids may likely be filtered through the soil or may settle in drain pipes (Montagne et al., 2009), soluble Si forms are exported from the soil profile with very few interactions with the soil solid phase. Si in soil water is generally considered as in soluble form with classical Si concentrations in soil waters ranging from 100 to 600 $\mu\text{mol L}^{-1}$ (Sommer et al., 2006; Cornelis et al., 2011). The Si concentrations measured in soil water in this study are thus at the low range of those classically encountered in soils. This form may moreover be favoured in the selected soil by the mineralogy of the weathered loess materials composed almost 80% of quartz, including in the lutum fraction. Quartz exhibits a large surface area which may facilitate its dissolution despite being a poorly soluble mineral. The Si concentrations in the sampled waters

are indeed often at equilibrium or oversaturated compared to quartz (the solubility of quartz being close to $100 \mu\text{mol L}^{-1}$). Such an equilibrium of soil water with quartz was also observed in another soil context (Lucas et al., 2012).

Hypothesizing that Fe and Al are mainly in colloidal forms at the event scale, the stability of the Al/Fe ratio around 4 in the drainage water (Figure 4A) suggests that colloidal forms of Fe and Al are not limited to peaks of drain discharge but concern the great majority of Fe and Al exports. The observation of a similar Al/Fe ratio of 4 in piezometer waters (Figure 4 B), at least for Eh values $> 300\text{mV}$, suggests that Fe and Al in piezometer waters are in colloidal form and that the Fe and Al exported from the soil profile originate from the E&Bt horizon. Although Fe^{2+} could not be analysed due to the low concentrations encountered in the sampled waters, increasing Fe concentrations in piezometer waters (Table 2) and decreasing Al/Fe ratios (Figure 4B) are interpreted as a selective increase in the concentrations of soluble Fe forms, for Eh below 300 mV. This suggests that the high concentrations of Fe, as observed in 2005 and 2006, may be due to the reductive solubilisation of Fe oxides (Hayes et al., 2000). Inglett et al. (2005) mentioned that facultative anaerobic bacteria that use NO_3 , Mn or Fe as electron acceptor are active in Eh conditions ranging from 100 to 300 mV. Such Eh conditions are typical of those encountered in this soil over the periods studied. Solubilisation of Fe oxides is moreover in good agreement with the formation of bleached soil volumes as a result of Fe reductive solubilisation and soluble translocation (Montagne et al., 2008; Cornu et al., 2012a; Montagne et al., 2016).

Such prolonged periods of reduction are sometimes followed by high Si concentrations recorded in the drain, as in spring 2005. These high Si concentrations are associated to high Eh and to a drop in pH from 10 to 6, which represents a huge proton production. Barbiero et al. (2010) demonstrated in neutral, Ca saturated Vertisols that such flushes in Si in soil water were promoted by ferrollysis. The Si solubilisation resulted from: i) the consumption of protons and

conversely the enrichment of the soil solution in alkalinity and base cations in the preceding reducing period; ii) the partial evacuation of alkalinity and base cations with the reduced soil solution, and finally iii) the hydrolysis of clay minerals or other Si-bearing minerals by the protons produced during the oxidation phase but not consumed by the alkalinity evacuated with reduced solutions. This process may also occur temporarily in the studied soil as at the end of the winter of 2005 (Figures 3) characterised by i) a drop in pH from 10 to 6, and ii) an increase in Si concentrations. Favouring the evacuation of the reduced solutions from the soil profile, the artificial drainage network may thus favour ferrollysis.

4.2. Element losses due to reducing conditions versus eluviation

Losses due to reducing conditions should release preferentially Fe and Mn while eluviation acts on Si and Al with a constant ratio.

Each year, 0.6 to 1 t ha⁻¹ of soluble and colloidal Si is exported from the soil profile (Table 3). The yearly losses as particles, due to clay translocation, were previously estimated by Montagne et al. (2016) at up to 5 t ha⁻¹ yr⁻¹ of the < 2 µm fraction. In line with Hardy et al. (1999), we considered that Si and Al concentrations in the lutum of loess-derived soils are about 20 and 10 g 100g⁻¹ respectively. We thus estimated that 1 t ha⁻¹ of Si and 0.5 t ha⁻¹ of Al are exported yearly as particles. Thus, the exports of Si by the drain in both colloidal and soluble forms are of the same order of magnitude as the exports as particles estimated by Montagne et al. (2016). Although the export of soluble Si is generally thought to be negligible for cold and temperate climates, the export of Si by drainage water is consistent with the rapid leaching of Si reported for example by Egli et al., (2001 and 2003) in Alpine soils or by those reported by Sommer et al. (2006) in a compilation for different soil types developed on granite and sandstone.

Considering Al, deposition and exports by the drain in soluble and colloidal forms are an order of magnitude lower than the Al exports as particles. Eluviation is thus the main process of Al losses from these soils.

Concerning Fe and Mn, the mass balance calculation shows an accumulation of the deposited elements in the soil profile (Table 3), while Montagne et al. (2008) observed from the solid phase analysis an accumulation of Mn but a loss of Fe. The accumulation of deposited Mn and Fe occurs mainly in the E&Bt horizon with the exception of the most reducing years for Fe (Table 3). The accumulation of Mn in the E&Bt horizon is in very good agreement with the higher Mn concentrations observed in this horizon than in the deeper soil horizons (Montagne et al., 2016) and provides a potential source contributing to Mn accumulations leading to the formation of the black impregnations (Cornu et al., 2012a; Montagne et al. 2013). It suggests that a significant contribution of the transport was in soluble form. The source of this Mn had not been identified so far.

The Fe situation is more complex: Montagne et al. (2016) demonstrated that Retisol evolution due to artificial drainage resulted in losses of Fe at both the E&Bt horizon and the profile scales, while we observed an accumulation of Fe, which ranged from 71 to 98 kg ha⁻¹ yr⁻¹ depending on the year (Table 3). Unaccounted exports as particles may explain part of the difference. Indeed, Montagne et al. (2016) estimated an average lutum loss of 5 t ha⁻¹ yr⁻¹. Considering this loss and the concentration of Fe in the lutum fraction (about 30 g kg⁻¹ after Montagne et al., 2008), we estimated that the average loss of Fe due to particle eluviation was about 600 kg ha⁻¹ yr⁻¹, largely exceeding the Fe deposited and accumulated in the E&Bt horizon. Nevertheless the Fe deposition, accumulated in the E&Bt horizon, may contribute to the formation of the so-called black concretions and impregnations (Montagne et al., 2008; Cornu et al., 2012a).

As a conclusion, loss of particles (the so-called eluviation process) seems to be the main soil evolution driving process responsible for the losses in Al and Fe from this drained Retisol profile. The importance of eluviation in artificially drained soil has already been shown in the literature with particle losses ranging from $1 \text{ kg ha}^{-1} \text{ yr}^{-1}$ (Sogon et al., 1999) to $5 \text{ t ha}^{-1} \text{ yr}^{-1}$ (Schwab et al., 1980; Montagne et al., 2016). However, eluviation is not the only active soil process as: i) the dissolution of Si from amorphous silica minerals like phytoliths, from quartz or from other Si-bearing minerals accounts for a non-negligible part of the Si losses from the soil profile; ii) Mn, and to a lower extent Fe, either deposited or released during reducing conditions, are involved in the formation of the black impregnations.

4.3. Dynamics and location of the processes considered

Reducing conditions occurred mostly from January to February but not every year. They only occurred after a sufficient period of soil water saturation, as already observed in both lab experiments (Quantin et al. 2001; Grybos et al., 2007; Cornu et al., 2009) and field monitoring (Vizier, 1971; D'Amore et al., 2004). This probably explained the absence of a reducing period in winter 2007 that, despite a high efficient rainfall (i.e., rain less potential evapotranspiration, Figure 2), experienced a limited drainage compared to the previous two years.

Although only observed in the most reducing years, the reductive solubilisation of Fe oxides for Eh values below 300 mV is attested by iron concentrations that are no longer linearly related to Al concentrations (Figure 4B). Part of Fe is thus probably released into solution due to the reduction of Fe oxides from the ochre volumes of the E&Bt horizon. This release contributes to the formation of the bleached, pale ochre and white-grey volumes as suggested by Montagne et al. (2008) and Cornu et al. (2012a). The released iron is then either precipitated as ferrihydrite in the black volumes or leached from the soil profile when the reducing conditions are strong

enough. This process does not occur every year, confirming the importance of extreme wet years on soil evolution as already demonstrated in other pedological contexts (Boulaine, 1978). In those years, the reducing period when strong enough as in winter 2005, is followed by an exceptional release of Si into the drain water that may be attributed, as discussed above, to a temporal activation of the ferrolysis process.

More water was sampled from the piezometers at 400 cm from the drain than closer to it. This may imply that reducing processes are more important far from the drain than close to it as already observed by Hayes et al. (2000) in the case of ditching and hypothesised by Montagne et al. (2013). Nevertheless no statistical difference in the chemical composition of the waters sampled by the piezometer was observed with the distance from the drain (Figure 6). This might be due to the fact that piezometers only sample free water that is homogenised at the horizon scale. At 400 cm from the drain, the soil is richer in clay minerals than at 60 cm according to Montagne et al. (2008), and reducing conditions may be more frequently encountered. If ferrolysis is confirmed in this soil, it may occur there.

5. Conclusion

In drained Retisols, which are classically drained in Europe when cropped, we have established that:

1- clay eluviation is responsible for losses of Al, Fe and partly Si and Mn from the soil, so that it may be considered as the main pedological driver of the current soil evolution;

2- dissolution of quartz and/or other Si-bearing minerals (phytoliths, clay minerals,...) results in dissolved Si losses from the soil with an intensity similar to losses by eluviation;

3- reducing conditions are likely not involved in exports from the soil profile but are responsible for the local redistribution of Fe and Mn and consequently for the particular differentiation of the E&Bt horizon, characteristic of Retisol;

4- bulk atmospheric depositions compensated the losses in some elements that are then accumulated in the E&Bt horizon as it is the case for Mn and Fe to a lesser extent. Longer chronicles of bulk atmospheric depositions are however mandatory to ascertain their past and future impact on soil evolution.

We also demonstrated the importance of extreme wet years in soil evolution on decade scale. Indeed, although only observed in the most reducing years, the reductive solubilisation of Fe oxides contributes to the differentiation of the E&Bt horizon and may be followed by exceptional Si losses due to the temporal occurrence of ferrollysis.

Lastly, we inferred from this study that the hierarchy of the soil processes driving pedogenesis is variable through time as a result of changes in environmental conditions. Typically an anthropic perturbation such as drainage increases particle losses and conversely decreases reducing conditions. In addition, the type of crop strongly impacts the water dynamic in soil and thus the potential occurrence of the reducing conditions. This impact of human actions on

soil evolution must thus be considered if we want to model soil evolution and predict the long-term delivery of soil services in a context of sustainable development.

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Table captions

Table 1: Main soil profile characteristics after Montagne et al. (2008) and Montagne and Cornu (2010).

Table 2: T-test for the Eh, pH and chemical composition of the anoxic and oxic piezometer waters considering a threshold of Eh of 300 mV for anoxic and oxic waters respectively. p-values are given for a 5 % confidence level.

Table 3: Mass balances of Al, Fe, Mn and Si for the entire soil profile and the E&Bt horizon for the three years studied. Losses by vegetation were estimated and not taken into account as they were found to be negligible for these elements.

Figure captions

Figure 1: Schematic representation of the evolution of the relative abundance of the different soil volumes with distance from the drain after Montagne et al. (2008). Location of the piezometers with respect to the drain.

Figure 2: For years 2005-2007: A- monthly rainfall (columns) and potential evapotranspiration (lines) in mm. Data are from the Meteo France Safran grid ; B- monthly drainage monitored at the outlet of the main drain in the field.

Figure 3: Drained water flow rate and associated pH (squares) and Eh (triangles) values measured at the outlet of the main drain. Horizontal lines represent the limit of oxic and reduced conditions.

Figure 4: Concentrations of Al and Fe: A- in the drainage, B- in the piezometer waters

Figure 5: Relationship between chemical composition of the drainage water and water flow .
A- Fe; B- Al; C-Mn; D- Si

Figure 6: Temporal course of Eh, pH and chemical composition of the piezometer waters at three distances from the drain.

Figure 7: Principal component analysis of the piezometer waters.

Figure 1: Schematic representation of the evolution of the relative abundance of the different soil volumes with distance from the drain after Montagne et al. (2008). Location of the piezometers with respect to the drain.

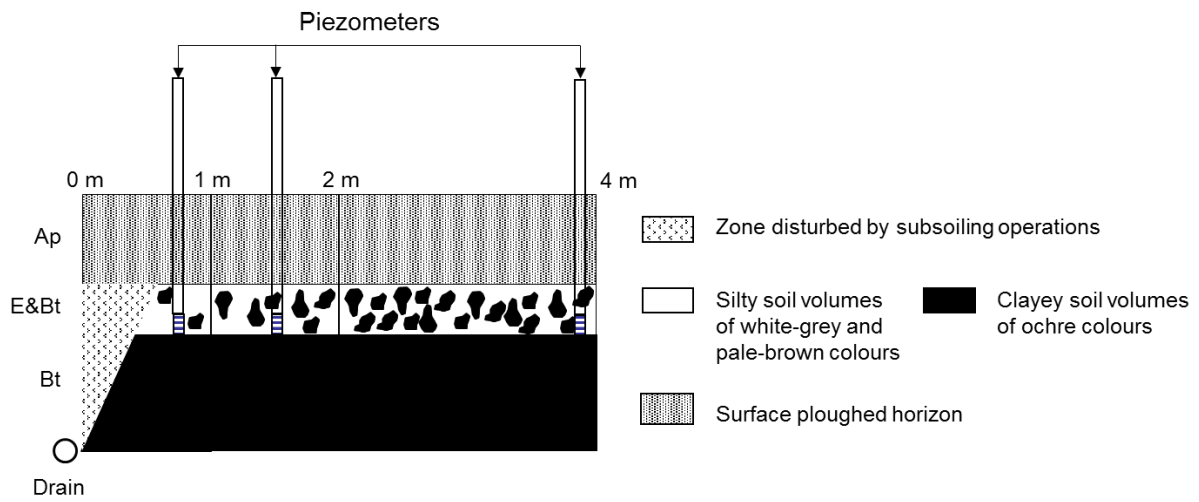
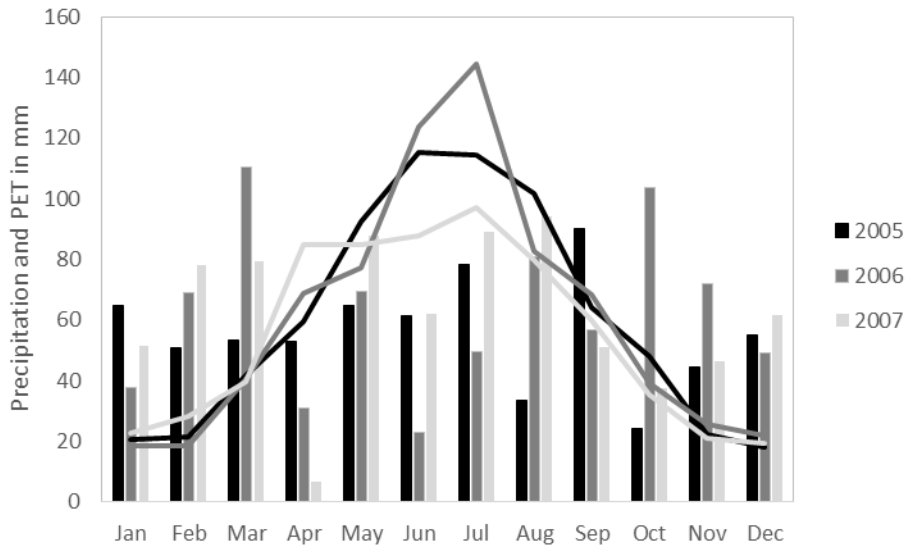


Figure 2: For years 2005-2007: A- monthly rainfall (columns) and potential evapotranspiration (lines) in mm. Data are from the Meteo France Safran grid ; B- monthly drainage monitored at the outlet of the main drain in the field.

A



B

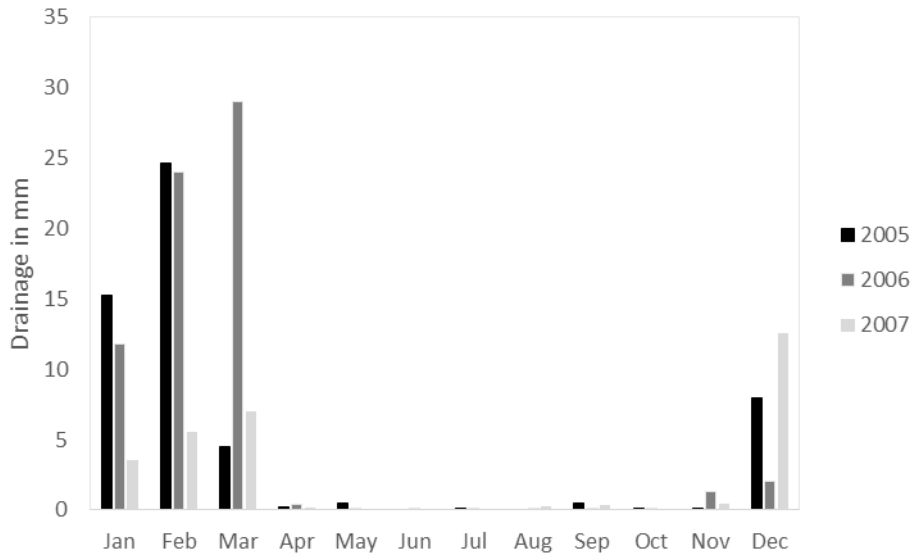


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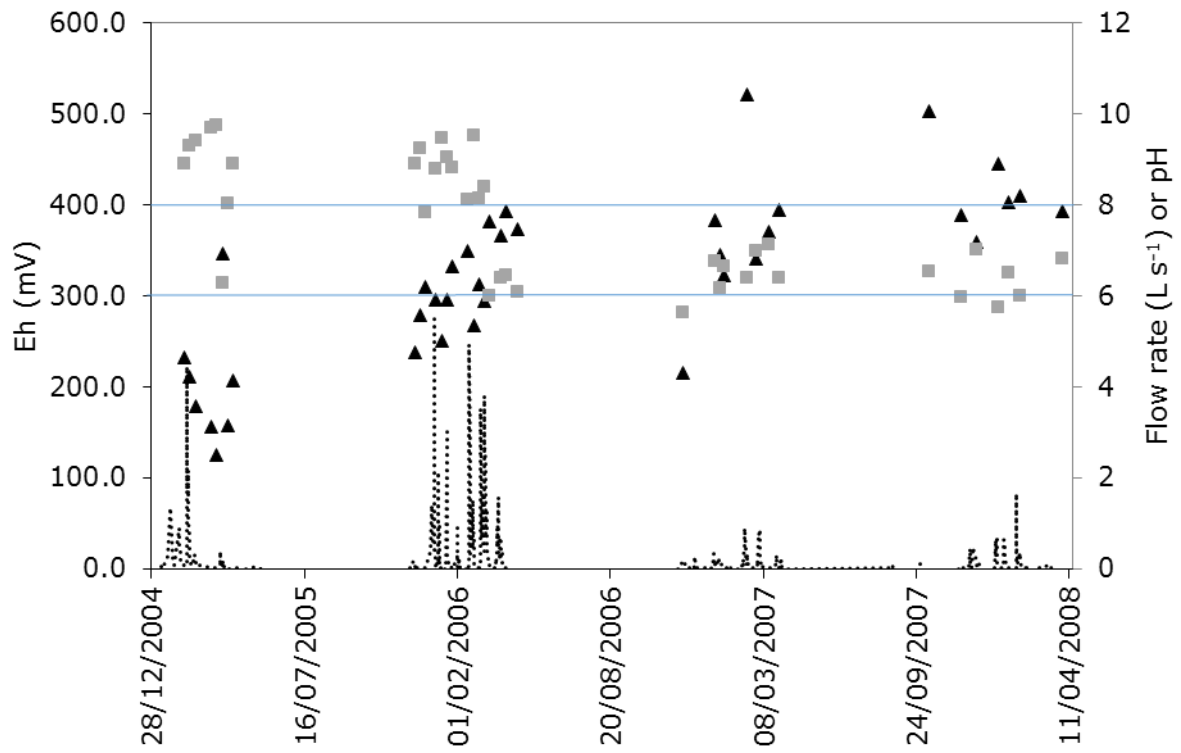
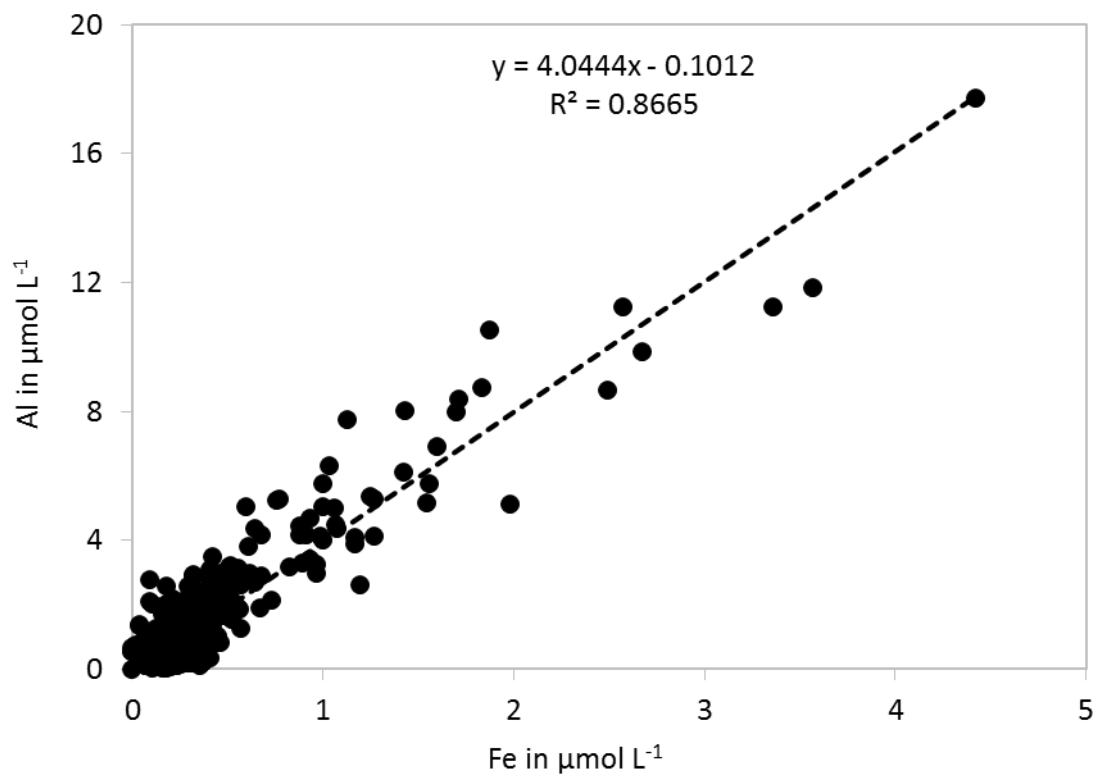


Figure 4: Concentrations of Al and Fe: A- in the drainage, B- in the piezometer waters

A



B

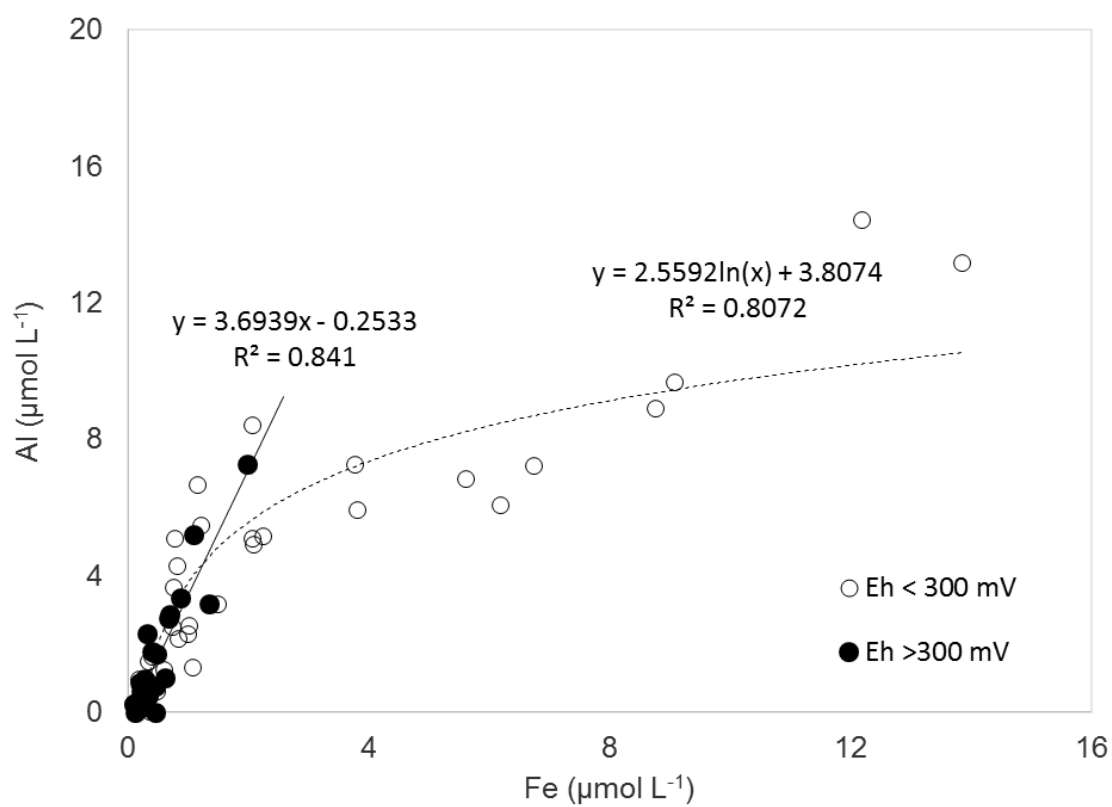


Figure 5: Relationship between chemical composition of the drainage water and water flow. A- Fe; B- Al; C- Mn; D- Si

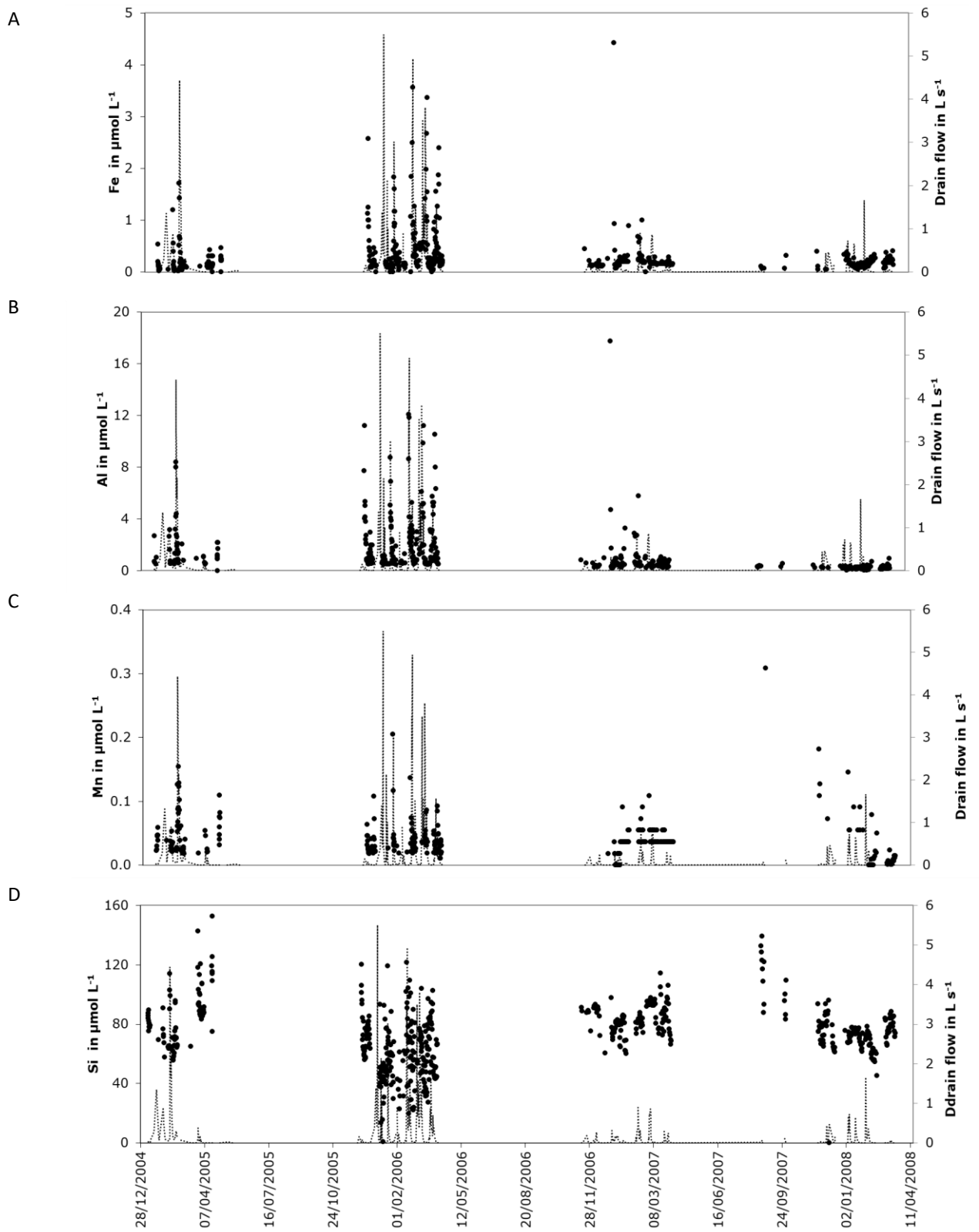


Figure 6: Temporal course of Eh, pH and chemical composition of the piezometer waters at three distances from the drain.

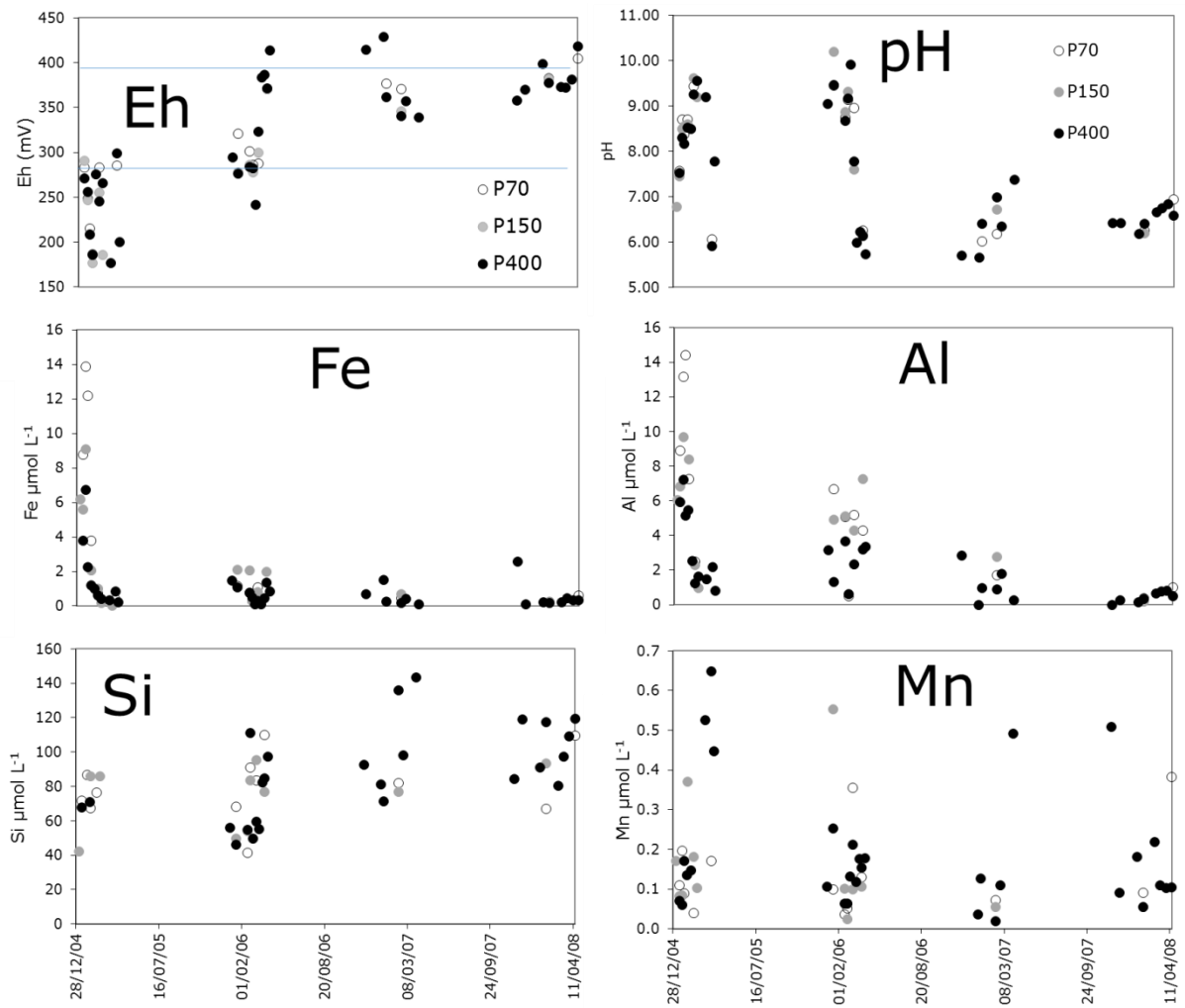


Figure 7: Principal component analysis of the piezometer waters.

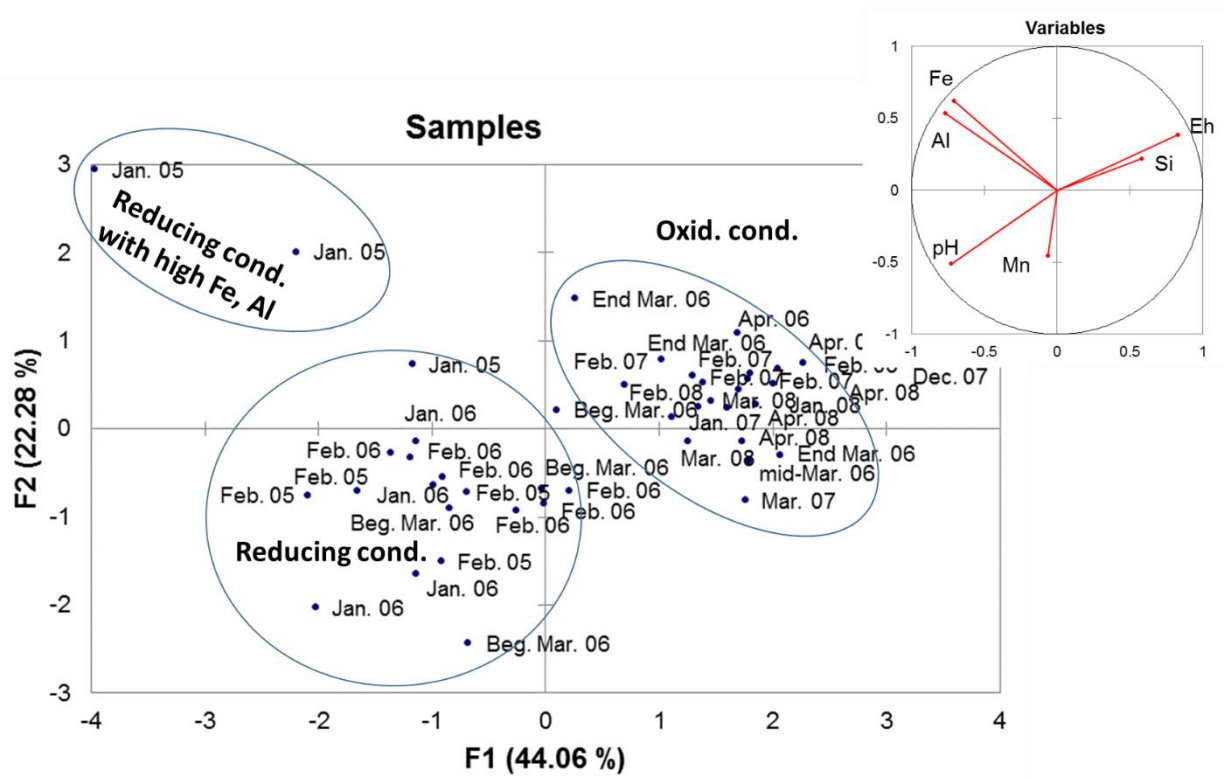


Table 1: Main soil profile characteristics after Montagne et al. (2008) and Montagne and Cornu (2010).

Distance to drain	Horizon names	Depth cm	Particle size (in μm) fractionation (g kg^{-1})					OC ----- g kg^{-1} -----	N_{tot}	pH_{water}	Fe	Mn	Al	Si	Ca
			<2	2-20	20-50	50-200	200-2000								
60 cm	Ap	10-20	133	365	372	51	79	7.61	0.78	7.7	1.60	1070	3.17	39	0.37
	E	20-35	135	360	381	53	71	7.94	0.82	7.8	1.50	1010	3.09	39	0.34
	Eg&Bt	35-45	162	383	359	42	54	1.73	0.26	8.1	1.56	659	3.57	39	0.30
	Eg&Bt	45-55	169	388	357	41	45	1.16	0.23	8.0	1.47	369	3.64	39	0.28
	Bt	55-65	263	354	312	37	34	1.23	0.25	8.0	2.53	626	4.92	36	0.37
	Bt	65-100	333	330	275	32	29	1.02	0.23	7.9	2.70	210	5.46	35	0.39
210 cm	Ap	10-20	138	362	367	54	79	7.19	0.77	7.5	1.48	1050	3.08	39	0.30
	E	30-40	140	364	376	51	69	6.76	0.73	7.8	1.60	1080	3.21	38	0.38
	Eg&Bt	40-50	280	342	298	34	46	1.59	0.31	8.0	2.68	786	4.87	35	0.38
	Eg&Bt	50-60	303	347	287	29	34	1.28	0.31	8.0	2.67	384	5.20	35	0.38
	Bt	60-70	328	336	276	29	31	1.19	0.27	8.1	2.88	403	5.78	35	0.43
	Bt	70-100	329	338	276	30	27	1.11	0.28	8.0	2.64	198	5.42	34	0.40
400 cm	Ap	10-20	132	365	381	53	69	6.99	0.71	7.4	1.47	999	3.14	38	0.38
	E	25-35	134	372	377	57	60	7.29	0.76	7.7	1.55	1160	3.14	40	0.39
	Eg&Bt	35-45	223	371	330	39	37	1.37	0.25	8.0	2.16	747	4.32	37	0.35
	Eg&Bt	45-55	288	333	309	38	32				2.67	430	5.17	36	0.35
	Bt	55-65	334	330	281	34	21	1.26	0.26	8.0	2.89	356	5.62	34	0.43
	Bt	65-100	334	325	284	32	26	0.93	0.25	7.4	2.81	226	5.49	35	0.39

1 Table 2: T-test for the Eh, pH and chemical composition of the anoxic and oxic piezometer waters
 2 considering a threshold of Eh of 300 mV for anoxic and oxic waters respectively. p-values are given
 3 for a 5 % confidence level.

	Water sample with				p-value
	Eh < 300 mV		Eh > 300 mV		
	n	mean	n	mean	
pH	35	8.6	27	6.4	< 0.0001
Fe ($\mu\text{mol L}^{-1}$)	34	2.57	25	0.57	0.008
Mn ($\mu\text{mol L}^{-1}$)	31	0.18	25	0.15	0.551
Si ($\mu\text{mol L}^{-1}$)	20	71	25	94	0.0004
Al ($\mu\text{mol L}^{-1}$)	32	4.2	22	1.2	0.001

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5 Table 3: Mass balances of Al, Fe, Mn and Si for the entire soil profile and the E&Bt horizon scale for
 6 the three years studied. Losses by vegetation were estimated and not taken into account as they
 7 were found to be negligible for these elements.

	Quantity	Fe	Mn	Al	Si	
		kg ha ⁻¹			t ha ⁻¹	
	mm	-----				
2005	Deposition	673	88 ± 50	40 ± 34	61 ± 47	0.1 ± 0.1
	Export at the E&Bt base	54	85 ± 34	5 ± 2	62 ± 25	1.1 ± 0.5
	Gain/losses from E&BT ^a		3 ± 50	36 ± 34	-2 ± 47	-1.1 ± 0.1
	Export by the drain	54	8 ± 1.6	1.2 ± 0.2	21 ± 4	0.7 ± 0.1
	Gain/losses from the soil ^b		79 ± 50	39 ± 34	40 ± 47	-0.6 ± 0.1
2006	Deposition	753	111 ± 30	64 ± 20	74 ± 33	0.1 ± 0.1
	Export at the E&Bt base	69	34 ± 13	5 ± 2	54 ± 22	1.4 ± 0.6
	Gain/losses from E&BT ^a		96 ± 19	70 ± 12	55 ± 22	-0.61 ± 0.05
	Export by the drain	69	40 ± 8	1 ± 0	70 ± 14	1 ± 0.2
	Gain/losses from the soil ^b		71 ± 30	63 ± 20	4 ± 33	-0.9 ± 0.1
2007	Deposition	746	101 ± 19	73 ± 12	60 ± 22	0.35 ± 0.05
	Export at the E&Bt base	30	4.9 ± 1.9	3.1 ± 1.2	5.1 ± 2.1	1 ± 0.4
	Gain/losses from E&BT ^a		96 ± 19	70 ± 12	55 ± 22	-0.61 ± 0.05
	Export by the drain	30	2.8 ± 0.6	0.4 ± 0.1	4.5 ± 0.9	0.6 ± 0.1
	Gain/losses from the soil ^b		98 ± 19	72 ± 12	56 ± 22	-0.22 ± 0.05

8

a- Gain/losses from E&BT horizon = Deposition - Export at the E&Bt base

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b- Gain/losses from the soil profile = Deposition - Export by the drain

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