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# ASSESSMENT OF VANADIUM DISTRIBUTION IN SHALLOW GROUNDWATERS

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## Abstract

Shallow groundwater samples (filtered at 0.2  $\mu\text{m}$ ) collected from a catchment in Western France (Petit Hermitage catchment) were analyzed for their major- and trace-element concentrations (Fe, Mn, V, Th and U) as well as their dissolved organic carbon (DOC) concentrations, with the aim to investigate the controlling factors of vanadium (V) distribution. Two spatially distinct water types were previously recognized in this catchment based on variations of the rare earth element (REE) concentrations. These include: (i) DOC-poor groundwater flowing below the hillslope domains; this type has low V contents; and (ii) DOC-rich groundwater originating from wetlands, close to the river network; the latter water type displays much higher V concentrations. The temporal variation of the V concentration was also assessed in the wetland waters; the results show a marked increase in the V content at the winter-spring transition, along with variations in the redox potential, and DOC, Fe and Mn contents.

In order to allow the study of organo-colloidal control on V partitioning in water samples, ultrafiltration experiments were performed at different pore size cut-offs (30 kDa, 10 kDa and 5 kDa). Two shallow, circumneutral waters were sampled: one was both DOC- and Fe-rich and the other was DOC-rich and Fe-poor. In terms of major- and trace-cations and DOC concentrations, the data were processed using an ascendant hierarchical classification method. This revealed the presence of two main groups: (i) a "truly" dissolved group (Na, K, Rb, Ca, Mg, Ba, Sr, Si, Mn, Co, Ni, Cr, Zn and Ni), and (ii) a colloidal group carrying DOC, Fe, Al, Pb, Cu, REE, U, Th and V. Vanadium has an unpredictable behaviour; it can be either in the organic pool or in the inorganic pool, depending on the sample.

Moreover, V speciation calculations - using Model VI and SCAMP - were performed on both samples. Speciation modelling showed approximately the same partitioning feature of these elements as compared to ultrafiltration data, namely: a slight change of the V speciation in groundwaters along the studied topographic sequence.

This implies that vanadium in hillslope groundwater wells occurs as a mixing of organic and

inorganic complexes, whereas V in wetland groundwater wells comprises mainly organic species. Using the dataset described above, factors such as aquifer-rock composition or anthropogenic input were demonstrated to probably play a minor role in determining the V distribution in shallow groundwaters. Although an anthropogenic impact can be ruled out at this local scale, we cannot preclude a perturbation in the global V cycle. Most likely, the two dominant factors involved are the organic matter content and the redox state either promoting competition with Fe-, Mn-oxides as V carriers in groundwater or not. In this context, it appears challenging to determine whether organic matter or redox-sensitive phases are the major V carriers involved, and a further study should be dedicated to clarify this partition, notably to address the processes affecting large-scale V transport.

## **1. Introduction**

Vanadium (V) is a naturally occurring element in air, soil, plants and water. Its average content in the earth's crust is approximately 0.0136% (Greenwood and Earnshaw, 1997). Vanadium in trace amounts represents an essential element for normal cell growth, but it may cause adverse effects when its concentration is much greater than a few tenths of  $\mu\text{g}$  per litre (Hope, 1997). Most data on the release of V into the environment have been related to industrial activities, especially from oil refineries and power plants using V-rich fuel oil and coal (e.g., Moskalyk and Alfanti, 2003 and references therein). Crude oil is enriched in V with respect to many other trace elements, with concentrations occasionally exceeding  $1 \text{ mg L}^{-1}$  (Hope, 1997). Thus, the fraction of dissolved V in surface waters might be an environmental indicator of oil combustion or pollution. Such pollution sources may be responsible for appreciable amounts of V into the environment, well above the natural background levels associated with rock weathering and sediment leaching (Hope, 1997; Lowenthal et al., 1992; Rühling and Tyler, 2001). Fluvial dissolved V concentrations might also be indicative of the types of rocks being weathered or, of

the nature of the weathering process. Shiller and Boyle (1987) presented an overview of the behaviour of dissolved V in rivers and estuaries. Shiller and Boyle (1987) and Shiller and Mao (2000) concluded that weathering rate and type of source rock, rather than solution chemistry or anthropogenic influences, appeared to be the important controlling factors on fluvial dissolved V concentrations.

Vanadium has several oxidation forms between -1 and +5. Vanadium(II) is particularly unstable in the environment (Wehrli and Stumm, 1989). Vanadium(III) is more stable than V(II), but it is also gradually oxidized by the air or dissolved oxygen. Vanadium(V) is expected to be the prevailing form in waters exposed to atmospheric oxygen, whereas V(IV) may be present in reducing environments. The oxidation rate of V(IV) to V(V) and the equilibrium between these two species in aqueous solution depend on several factors, such as pH, V concentration, redox potential, the ionic strength of the aqueous system and biological activity (e.g., Wang and Sanudo Wilhelmy, 2009). In water, V(IV) is commonly present as a vanadyl cation [ $\text{VO}^{2+}$ ,  $\text{VO}(\text{OH})^+$ ], whereas V(V) exists as a vanadate oxyanion ( $\text{H}_2\text{VO}_4^-$ ,  $\text{HVO}_4^{2-}$ ) (Wanty and Goldhaber, 1992).  $\text{VO}^{2+}$  is strongly adsorbed on solid phases, including organic and oxyhydroxide phases (Wehrli and Stumm, 1989). Adsorption of anionic V ( $\text{H}_2\text{VO}_4^-$ ,  $\text{HVO}_4^{2-}$ ) is much lower than the cations; however,  $\text{VO}^{2+}$  solubility may be greatly increased through complexation with organic matter (Lu et al., 1998; Szalay and Szilagyi, 1967). While V(IV) is not thermodynamically stable at  $\text{pH} > 7$ , complexation by various organic and inorganic species may considerably increase its stability (Wanty and Goldhaber, 1992). Eventually, the V(V) oxidation state ion is more toxic than the V(IV) ion (Hope, 1997; Hope, 2008).

A recent study on the geochemistry of V has emphasized the redox features of this element (Wright and Belitz, 2010), which makes it more soluble in oxidizing waters than in reducing waters (Wehrli and Stumm, 1989). As a consequence, fluvial dissolved V concentrations might be an indicator of inputs from reducing sources within river drainage systems (Shiller, 1997; Sugiyama, 1989). Additionally, this difference in solubility appears to be

an important contributing factor to the enrichment of V in organic-rich reducing sediments (Breit and Wanty, 1991). Other studies have investigated V geochemistry as a potential paleoceanographic tool. For example, Francois (1988) and Calvert and Pedersen (1993) examined the V accumulation in sediments as an indicator of past reducing conditions in specific oceanic regions. Hastings et al. (1996) have also evaluated the incorporation of V into biogenic carbonate phases as a possible indicator of the past oceanic conditions. Seeking a better understanding of the processes that result in V removal into organic-rich sediments, Emerson and Huested (1991) assessed V distributions in oxygen-depleted present-day natural waters. They found that dissolved V concentrations were generally lower in anoxic basins than in oxic seawater, due to V removal into anoxic sediments. In addition to the study by Emerson and Huested (1991), other authors (e.g., Szalay and Szilagyi, 1967) have suggested that organic matter may play a role in modifying vanadium's redox behaviour through the reduction of V(V) by humic acid and by the competition of organics with solid surfaces for V(IV). However, in order to explain oceanic changes in terms of dissolved V, the processes majorly affecting the oceanic sources of this element must also be understood (i.e., rivers, groundwaters). This study reports temporal and spatial variations of V shallow groundwaters from wells located along a transect set perpendicular to the topographic slope (hereafter denoted as toposequence) set up in a small catchment in France. Ultrafiltration and speciation modelling of representative samples of this toposequence, using the Windermere Humic Aqueous Model (WHAM) including both Humic Ion-binding Model VI (Tipping, 1998) and the Surface Chemistry Assemblage Model for Particles (SCAMP; Lofts and Tipping, 1998), are also presented. Such modelling permits the calculation of equilibrium chemical speciation for waters in which natural organic matter plays a significant role. The catchment studied here was chosen as a suitable site for V investigation because information in terms of hydrogeology, hydrochemical and trace elements such as rare earth elements (REE) settings is already available (Clément et al., 2003; Gruau et al., 2004). In this context, the main aims of this work are to address the respective influence of

source-rock composition, redox changes and organic matter on the distribution of V in shallow groundwaters.

## 2. Material and methods

### 2.1 Site description

The study was conducted between winter 1998 and spring 2004 in a riparian ecosystem (the “*Le Home*” toposequence) located along a small tributary (Petit Hermitage Creek) in western France (48.3°N, 1.3°W), at an altitude of ca. 20 m above sea level (Fig. 1). The study site was located within a 14 km<sup>2</sup> drainage basin. The region has an oceanic climate characterized by mild, humid weather throughout the year. Annual rainfall ranged between 850 and 900 mm during the study period. The mean discharge of the stream is approximately 90 L s<sup>-1</sup>. The stream hydrological regime is characterized by low permanent flow during dry periods (i.e., late spring and summer), and rapid and significant flood events during high water periods (i.e., late winter and early spring). The upland-riparian boundary is characterized by a steep 2–3 m drop in elevation from the surrounding fields into the riparian ecosystem (Fig. 1). The catchment drained by the riparian wetland is mainly agricultural with crops and grass fields for cattle. At the time of the study, the eastern part of the upslope was under perennial grassland mown for hay and grazed by suckling cows and calves for only a few weeks per year. The western part of the upslope was a crop field (maize/wheat) with intensive agricultural practices. Fertilizer application rates were high, [N]<sup>3</sup> 200 kg ha<sup>-1</sup> year<sup>-1</sup>, which resulted in high groundwater NO<sub>3</sub><sup>-</sup>-N concentrations ranging from 10 to 20 mg L<sup>-1</sup> (Clément et al., 2003; Gruau et al., 2004). The geological substratum of the catchment is granite in the upstream part (Villegartier Forest) and micaschist (Proterozoic schist) in the downstream part where the study site is located. Compared to the deeper fresh rocks, the upper 10-20 m have been weathered into a higher clay content. The wetland is filled with late Phanerozoic clay-rich alluvium.

## 2.2 Sampling and field measurements

Wetland groundwater samples (F14 well) were recovered weekly from January 1999 to June 1999 for the temporal and spatial variation study. Groundwater samples flowing below the upland/wetland transition zone (F5 and F7 wells) were collected twice, in February 1998 and January 1999, while the upland P11 well was sampled only once, in January 1999 (Fig. 1). Wetland groundwaters (F14 well) and other samples flowing below the upland/wetland transition zone (F7 well) were sampled in November 2004 for the ultrafiltration experiments. These water samples were immediately filtered on site using 0.2  $\mu\text{m}$  cellulose acetate filters. Filters were pre-cleaned with ultrapure water to prevent any contamination (Bouhnik-Le Coz et al., 2001; Petitjean et al., 2004). Temperature, pH and Eh were measured on site. The pH was measured with a combined Sentix 50 electrode; the accuracy of the pH measurement is  $\pm 0.05$ . Eh was measured using a platinum combination electrode (Mettler Pt 4805). Electrodes are inserted into a cell constructed to minimize diffusion of atmospheric oxygen into the sample during measurement. Eh values are presented in millivolts (mV) relative to the standard hydrogen electrode. The accuracy of Eh measurement is  $\pm 5$  mV.

## 2.3 Ultrafiltration set-up description and chemical analyses

Ultrafiltration experiments were performed on two samples recovered from the F7 and F14 wells using 15 mL centrifugal tubes (Millipore Amicon Ultra-15) equipped with permeable membranes of decreasing pore sizes of 30 kDa, 10 kDa, and 5 kDa (1 Da = 1 g mol<sup>-1</sup> for H) for the separation of the colloidal bound elements. Metal-colloid complexes are retained by the ultrafiltration membrane, whereas free ions and smaller chemical complexes pass into the ultrafiltrate. The degree of metal-colloid complexation is usually determined from the metal concentration in the ultrafiltrate relative to the original solution. Each centrifugal filter device



was washed and rinsed with HCl 0.1 mol L<sup>-1</sup> and ultra-pure (MilliQ) water two times before use. The starting filtrates were passed through a 0.2 µm filter, and then aliquots of these filtrates were passed through membranes of smaller sizes. All ultrafiltrations of the 0.2 µm filtrates were done in parallel. The centrifugations were performed using a Jouan G4.12 centrifuge equipped with a swinging bucket rotor at about 3,000 g for 20 minutes for the 30 kDa and 10 kDa filters and 30 minutes for the 5 kDa filters, respectively. All experiments were carried out at room temperature (~20 ± 2°C).

Major cations and trace elements concentrations were determined by ICP-MS (Agilent Technologies HP4500) at the University of Rennes 1. Quantitative analyses were carried out by external calibration (three points) by using mono- and multi-element standard solutions (Accu Trace Reference, USA) with major- and trace-element concentrations similar to that of the analyzed samples. Indium was used as an internal standard at a concentration of 100 µg L<sup>-1</sup> in order to correct for instrumental drift and matrix effects. The measurement bias for the determination of the concentration of major- and trace-elements was assessed in a previous work by the analysis of the SLRS-4 certified reference material (river water); a bias < 2% was obtained for all analytes (Pédrot et al., 2008; Pourret et al., 2007b; Yeghicheyan et al., 2001). Dissolved organic carbon concentrations were determined using a Shimadzu 5000 TOC analyzer (Université de Rennes 1). A measurement bias of ± 5% was obtained by the analysis of a freshly prepared standard solution of potassium biphtalate. Total alkalinity was determined by potentiometric titration with an automatic titrating device (794 Basic Titrino Methrom). Major anion (Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup> and NO<sub>3</sub><sup>-</sup>) concentrations were measured by ionic chromatography (Dionex DX-120) with a bias below 4%. Carbonate alkalinity was determined by potentiometric titration with an automatic titrator (Basic Titrino Metrohm).

It is worth noting that the ultrafiltration procedure prevents the calculation of the mass balance using the ratio between the filtrate and the retentate because the retentate volumes are limited (0.2 mL). However, as the same material was used for all filtrations, molecular size

exclusion rather than adsorption onto membranes should control the colloid distributions between ultrafiltrates.

In our study, all ultrafiltrations were performed in duplicate. A good repeatability was observed for DOC and both major and trace element concentrations. The relative difference between duplicates was generally  $< 5\%$  for most elements except for some trace elements in the lower pore size cut-off fraction (i.e., in the  $< 5$  kDa fraction, about  $10\%$ ). Further information on the ultrafiltration procedure can be found in Pourret et al. (2007b). The possible adsorption of major and trace inorganic species onto the membrane or cell walls was also monitored. For this purpose, inorganic multi-element standard solutions - whose concentrations were representative of that of the studied groundwaters - were ultrafiltered several times (Pourret et al., 2007b). The results showed that between  $92.99\%$  (for Pb) and  $99.99\%$  (for Mg) of the major- and trace-elements present in solutions were recovered in the ultrafiltrates ( $96.13\%$  for V), demonstrating that neither the major nor trace elements were adsorbed onto the membranes or walls of the cell devices.

In order to lessen the cross-contamination of any of the analytical steps (sampling, filtration, storing and analysis), the samples were stored in acid-washed Nalgene polypropylene containers before analyses. The blank levels were lower than  $2\%$  of the measured concentrations for all studied elements, except for DOC ( $< 6\%$ ).

## 2.4 WHAM 6, Model VI and SCAMP description

WHAM 6 (version 6.0.10) was used to calculate V speciation. Predictions for the equilibrium metal binding by environmental colloids made for the present study were done using the combined WHAM-SCAMP speciation code. WHAM-SCAMP is able to provide a full description of solid-solution speciation by incorporating two main codes: (1) the Windermere Humic Aqueous Model (WHAM) to calculate the equilibrium solution speciation (Tipping,

1994), and (2) the Surface Chemistry Assemblage Model for Particles (SCAMP) to calculate the binding of protons and metals by natural particulate matter (Lofts and Tipping, 1998). The code for the WHAM model incorporates a number of submodels: Humic Ion-Binding Model VI and a description of inorganic solution chemistry, cation exchange by clays, the precipitation of aluminium and iron oxyhydroxides, and adsorption-desorption of fulvic acids. The SCAMP model consists of three submodels: (1) Humic Ion-Binding Model VI, (2) a SCM describing proton and metal binding to oxides (i.e.  $\text{AlOx}$ ,  $\text{SiOx}$ ,  $\text{MnOx}$  and  $\text{FeOx}$ ), and (3) a model describing the electrostatic exchange of cations on clays.

Model VI, a discrete binding site model in which binding is modified by electrostatic interactions, was described by Tipping (1998; 2002). It is worth noting that there is an empirical relationship between the net humic charge and an electrostatic interaction factor. The discrete binding sites are represented by two types of sites (A and B) and within each site type, there are four different sites present in equal amounts. The two types of sites are described by intrinsic proton binding constants ( $\text{pK}_\text{A}$  and  $\text{pK}_\text{B}$ ) and spreads of the values ( $\Delta\text{pK}_\text{A}$  and  $\Delta\text{pK}_\text{B}$ ) within each site type. There are  $n_\text{A}$  ( $\text{mol g}^{-1}$ ) A-type sites (associated with carboxylic type groups) and  $n_\text{B} = n_\text{A}/2$  ( $\text{mol g}^{-1}$ ) B-type of sites (often associated with phenolic type groups). Metal binding occurs at single proton binding sites or by bidentate complexation between pairs of sites depending on a proximity factor that defines whether pairs of proton binding groups are close enough to form bidentate sites. Type A and Type B sites have separate intrinsic binding constants ( $\log K_\text{MA}$  and  $\log K_\text{MB}$ ), both of which are associated with a parameter,  $\Delta\text{LK}_1$ , defining the spread of values around the medians. A further parameter,  $\Delta\text{LK}_2$ , takes into account a small number of stronger sites. By considering results from many datasets, a universal average value of  $\Delta\text{LK}_1$  is obtained, and a correlation is established between  $\log K_\text{MB}$  and  $\log K_\text{MA}$  (Tipping, 1998). Then, a single adjustable parameter ( $\log K_\text{MA}$ ) is necessary to fully describe the metal binding. The generic parameters for HA are presented in Table 1. WHAM 6 databases were modified by including  $\log K_\text{MA}$  for  $\text{V(IV)O}$  complexation with fulvic and humic acids (Tipping, 2002) and well-accepted,

infinite dilution (25°C) stability constants for V(IV)O inorganic complexes (Wanty and Goldhaber, 1992 and references therein).

The SCAMP model (Lofts and Tipping, 1998) was also modified to include V species, as well as Fe, Mn and Al oxides. Briefly, SCAMP describes the equilibrium adsorption of protons and metals by natural particulate and colloidal matter using a combination of submodels for individual binding phases. Interactions with natural organic matter are described with Model VI, and adsorption by oxides with a surface complexation model that allows for site heterogeneity. An idealized cation exchanger is also included. SCAMP uses published parameters for Model VI, and the parameters for the oxide model are derived from published data for proton and metal binding by oxides of Al, Si, Mn, and Fe(III) (Table 2).

## 2.5 Data treatment

The ascending hierarchical classification using Ward's criterion was performed through XLSTAT so as to implement sample classification. This method is based on squared Euclidian distances between individuals in the space formed by the available variables. The initial sample is partitioned into several classes of individuals so as to maximize interclass inertia (i.e., to maximize variability between groups) and minimize intraclass inertia (i.e., to maximize homogeneity in each group). As for the factor analysis, the raw data matrix was introduced in the principal component analysis, without any rotation. The input data are the whole set of ultrafiltrates after each cut-off for all considered elements, as in Pourret et al. (2007b) and Pédrot et al. (2008).

## 3. Results

Measured concentrations of major and trace elements are reported in Table 3. The major and trace element data recovered after the filtration and ultrafiltration experiments will be discussed in the following section.

### 3.1 Temporal and spatial variation

The analytical data are reported in Table 3 and allow the recognition of two distinct groups of waters based on their spatial location. All data, except for V, have already been published elsewhere (Gruau et al., 2004).

#### *3.1.1 Hillslope groundwaters*

This first group - hillslope groundwater - corresponds to waters collected below the upland domain (P11 well) and below the upland–wetland transition zone (F5 and F7 wells). These waters display slightly acidic pH, low DOC, moderate to high  $\text{NO}_3^-$  concentrations, and low to very low REE, Th, U, Mn and Fe levels (Gruau et al., 2004; Table 3). Vanadium concentrations are also very low (Table 3). The most striking feature is the increasing V concentrations from upland to hillslope from  $0.32 \mu\text{g L}^{-1}$  to  $1.42 \mu\text{g L}^{-1}$ . This spatial variation is followed by temporal variation from  $0.35 \mu\text{g L}^{-1}$  to  $0.78 \mu\text{g L}^{-1}$  and from  $0.95 \mu\text{g L}^{-1}$  to  $1.42 \mu\text{g L}^{-1}$  for the F5 and F7 wells, respectively.

#### *3.1.2 Wetland groundwaters*

The water samples of this group are restricted to wetland well F14 and have high to very high DOC contents (ranging from  $7.98 \text{ mg L}^{-1}$  to  $53.10 \text{ mg L}^{-1}$ ), high REE, Th, U, Mn and Fe concentrations, and low to very low  $\text{NO}_3^-$  concentrations (Gruau et al., 2004). Vanadium

concentrations are also high and the range of V concentrations ( $1.25 \mu\text{g L}^{-1}$  to  $12.20 \mu\text{g L}^{-1}$ ) is large with values considerably higher than those reported for average world rivers ( $0.76 \mu\text{g L}^{-1}$ ; Johannesson et al., 2000).

Systematic seasonal concentration changes are evidenced in these waters. As shown in Fig. 2, concentrations were rather low in January and increased markedly with the beginning of February until the middle of March, then showing an irregular decline from April to June 1999. Comparison of V data with Fe, Mn, DOC concentrations and redox potential results shows that the onset of V release at the end of January was concurrent with a decline of the redox potential (Fig. 2b, c) and coincides with an increase in DOC and both Mn and Fe concentrations (Figs. 2a, b, c and 3).

### 3.2 Ultrafiltration

In order to establish the role of organic colloids in the colourless, DOC-poor part of the *Le Home* water table and in DOC-rich water, hillslope and wetland groundwater samples (i.e., F7 and F14 wells) were successively filtered through membranes of smaller pore size (i.e., 30 kDa, 10 kDa and 5 kDa; see Table 4). Vanadium concentrations decrease upon successive filtrations at decreasing pore size (Figs. 5 and 6). These results illustrate differences with regards to the colloidal and dissolved partitioning of V in these two samples. Two clusters corresponding to common elemental distribution in the two samples were identified through the ascending hierarchical classification (Fig. 3), as following:

#### (i) cluster I: "truly" dissolved behaviour

Concentrations of Rb and alkaline metals such as Na and K are not affected by ultrafiltrations since no fractionation - following the decreasing pore sizes or the DOC concentrations - theoretically occurs. Alkaline elements behave as "truly" dissolved in the form of inorganic species as often reported in the literature (e.g., Pokrovsky and Schott, 2002). The

concentrations of major- and trace-alkaline metals (Ca, Mg, Rb, Sr and Ba) do not change significantly during filtration. Silica concentrations display no significant variations in the successive filtrates. This suggests that aqueous silica is not trapped by organic colloids and/or by small-size clay minerals or phytolites. Cobalt, Ni, Cr, Mn, Zn concentrations do not exhibit large variations through the different decreasing pore size cut-offs suggesting that these transition metals have to be mostly present as "truly" dissolved species or small size inorganic complexes (e.g., Gaillardet et al., 2003).

(ii) cluster II: colloidal pool-borne elements

Copper, REE, Pb, Th and U concentrations display extremely regular positive correlations versus DOC concentrations for both samples. The linear relationships (see Table 4) suggest that these trace elements are strongly bound to organic matter and probably complexed to very low molecular weight organic ligands such as extracellular ligands, as well as larger size colloids such as fulvic and/or humic acids, cell fragments or bacteria as elsewhere reported (e.g., Sigg et al., 2000; Pourret et al., 2007b). Aluminium and Fe concentration variations through successive filtrations suggest that: (i) these elements do not occur as free species in solution, and (ii) two types of colloids can carry these metals (i.e. Al-, Fe-rich inorganic colloids or organic-, Al-, Fe-complexing colloids). This indicates a major control of Al by inorganic mixed Fe/Al oxyhydroxides. Moreover, as shown in Pourret et al. (2007b), V displays an unpredictable behaviour with regards to the considered sample.

*3.1.1 Hillslope groundwaters (F7)*

Dissolved V was found to be associated with Fe colloids as their concentrations sharply decrease with decreasing pore size from 0.2  $\mu\text{m}$  to 30 kDa (Fig. 5). It has been argued that dissolved V in rivers draining silicate rocks originates from silicate weathering (Shiller and Mao, 1999; Shiller and Mao, 2000). However, no correlation was observed between dissolved Si and V

in the studied samples. The presence of high amounts of colloidal Fe in these rivers, which serves as a potential V carrier, is likely to hide the different silicate vectors of V. The vanadium concentration displays a positive relationship with the DOC concentration, suggesting that the ability of V to form complexes with organic colloids remains constant over the molecular size range of the available colloid materials. The decrease following the lowering of the DOC concentrations suggests, on one hand, that for the uppermost sample, V is still carried by the organic phase (low- and high-molecular weight), and on the other hand, the decrease of V concentrations follows the same trend as that for Al. This suggests that V concentrations in such groundwater are controlled by mixed DOC/Al-rich phases, regardless of the pore size cut-off. Moreover, the large decrease of V concentrations following that of Fe between 0.2  $\mu\text{m}$  and 30 kDa suggests, as earlier reported, that Fe-rich phases exert significant control on the speciation of V at this cut-off. At lower filtration sizes, V concentrations tend to be the lowest concentrations ( $0.15 \mu\text{g L}^{-1}$ ), suggesting that V is also carried by a mixed Al/DOC-rich phase (Fig. 5).

### 3.2.2. Wetland groundwaters (F14)

Vanadium concentrations display a large drop between 0.2  $\mu\text{m}$  and 30 kDa filtrations (Fig. 6), which may imply that a significant fraction (about 55%) of V is carried by large-size colloids. When looking at the lower cut-off data, the strong decrease in the first filtration step implies that V is strongly bound to high-molecular weight organic material. The nearly constant V concentration after the 30 kDa filtration implies that V behaves more independently of DOC (Fig. 6). Moreover, the V concentration pattern is different than that of the more DOC-depleted sample with far less variation regarding the Fe concentrations after 30 kDa filtration. This suggests that V should be partly carried by a Fe-rich phase. In addition, Fe concentrations strongly decrease with respect to the high molecular organic colloids (~80% in the > 30 kDa fraction) similarly to V, hence implying that V could be carried by mixed Fe-C phases.



Furthermore, when comparing the behaviour of V with respect to Al and Fe with that in the ultrafiltered DOC-depleted sample recovered from the hillslope (F7), we note that whereas V concentrations after the 30 kDa filtration follow the same trend as the Al and Fe concentrations in the wetland sample, V concentrations in the hillslope sample is mostly correlated with Al, but to a lesser extent with Fe. This latter point suggests that Fe and Al behave differently with regards to V in wetland and hillslope groundwater; low-molecular weight Fe compounds in the hillslope groundwater probably transport less V.

### 3.3 Speciation calculation using Model VI

Model VI and SCAMP included in WHAM 6.0 were used to calculate V speciation in groundwaters from the F7 and F14 wells. The modelling results were compared with the experimental data presented above. Major cations and anions were considered, as well as Fe and Al, for calculating the V speciation of the studied samples (see Table 4). In WHAM 6.0 (Lofts and Tipping, 1998), neither oxide precipitation nor redox reaction occur, so only complexation in solution is modelled by our speciation calculation. The assumption that 50% of the DOM is active as HM in our samples (Thurman, 1985), of which 80% is present as HA and 20% as FA (Viers et al., 1997), was chosen. More details on the "active" DOM parameter can be found in Pourret et al. (2007a; 2010). Aluminium colloids as well as Fe oxides were also considered (Lofts and Tipping, 1998). The speciation modelling results are displayed in Table 5.

Consistently with the ultrafiltration results, speciation calculations show that organic V species are the dominant species in the F7 groundwater (i.e., 47% complexed with HA and 47% with FA). The remaining V is present as  $V(IV)O^{2+}$  (6%) (Table 5). In the F14 groundwater sample, the inorganic proportion of V is lower (i.e., only 1%). Speciation calculations show that organic V species are also the dominant species in the F14 groundwater (i.e., 58% complexed with HA and 41% with FA) (Table 5). Therefore, as with the ultrafiltration results, the speciation

modelling calculations illustrate a slight change of the V speciation in groundwaters along the *Le Home* transect. Vanadium in the hillslope groundwaters wells occurs as a mixing of organic and inorganic complexes, whereas V in the wetland groundwaters wells comprises mainly organic species. It is worth to underline that the modelling calculation and ultrafiltration results both conclude that the downhill decrease in inorganic complexation occurs in phase with a progressive scavenging of the V by a colloidal organic pool.

## **4. Discussion**

### **4.1 Approach limitation**

The authors of the WHAM-SCAMP model have noted a number of possible pitfalls in its application (Lofts and Tipping, 1998); the major ones are as follows: (i) the application of the WHAM-SCAMP model relies upon consistency between the metal binding data obtained for laboratory prepared phases and the metal binding properties of component phases found in natural colloidal assemblages; (ii) the surface complexation modelling technique is difficult to adapt in order to obtain model parameters from experimental Mn oxide data available in the literature (e.g., Dzombak and Morel, 1990; Kosmulski, 2006); (iii) there is some evidence in the literature that component phases constituting natural particulate materials are intimately associated (Peacock and Sherman, 2004); and (iv) ternary surface complexes are not considered even if it has been shown that Fe-rich organic colloids may adsorb metal ions (Buffle et al., 1998; Fein, 2002; Hiemstra and Van Riemsdijk, 1999; Schindler, 1990). These types of associations have implications when considering the validity of the modelling approach, which relies upon the assumption that the components of the colloidal assemblage exist as discrete phases. Lofts and Tipping (1998) note that these associations can lead to a deviation from the additivity of metal

binding expected from a simple combination of isolated phases such as DOC-rich colloids, and Mn and Fe oxyhydroxides.

Vanadium(IV) may account for more than 50% of the total dissolved V in mildly reducing groundwaters (Bosque-Sendra et al., 1998; Elbaz-Poulichet et al., 1997; Emerson and Husted, 1991). Both the oxidation rate from V(IV) to V(V) and the coexistence of the two species in aqueous solution depend on the pH, V concentration, reduction-oxidation potential and ionic strength of the system (Fig. 7). Even if V(IV) is not thermodynamically stable above pH 7, complexation by various organic and inorganic species may considerably increase its stability (Lu et al., 1998; Szalay and Szilagyi, 1967; Tribouvillard et al., 2006; Wanty and Goldhaber, 1992). Thus, V(IV) has only been considered in a speciation calculation performed using the WHAM-SCAMP model, considering a pH below 7 and DOC concentrations ranging between 11.1 and 21.5 mg L<sup>-1</sup>.

Although the 5 kDa cut-off allows very small size colloids to remain in solution, the lack of integration of adsorption processes onto inorganic species, as well as the coprecipitation of inorganic species appear to be the major causes of divergence between ultrafiltration data and speciation calculations for V. It is then important to be aware that this type of model does not take into account any uptake of metals resulting from competitive reactions between Fe-rich and DOC-rich colloids and that the occurrence of ternary surface complexes is thus not considered.

The studied samples are organic-rich groundwaters with an organic pool that seems to be in excess with regards to the metals available for complexation. However, this kind of competition (i.e., ternary surface complexes) is still difficult to interpret using only ultrafiltration data. Cation ligand complexes can be adsorbed onto solid particles to form ternary surface complexes either as a cation linked to the mineral surface over the ligand or as a ligand linked to the surface over the cation (Buerge-Weirich et al., 2002). As an example, relatively recently published data on REE (Davranche et al., 2008) showed the impact of ternary surface complexes (humates/oxyhydroxides/REE) on metal speciation. Thus, it appears necessary for speciation

models to take processes such as adsorption onto Mn and Fe oxyhydroxides into account - considering that the lack of such a reaction precludes any true speciation to be assessed - as the competition between Fe and C-based colloidal carriers is required for constraining element geochemical cycles or element fate in polluted environments. Apart from this, such a modelling approach is not intrinsically incorrect (Zhu and Anderson, 2002); these values may well be the best possible overall values even if they cannot be extrapolated to all applications.

## 4.2 Colloid-mediated control on V distribution in shallow groundwaters

It is now widely accepted that the colloidal phase plays a significant role in the transport and cycling of trace metals in water as assessed here for V, as it has already been illustrated for REE on this catchment (Gruau et al., 2004; Pourret et al., 2007a). Colloid-mediated carriage of V has been well described (Dupré et al., 1999; Gaillardet et al., 2003; Lyvén et al., 2003; Pokrovsky et al., 2005; 2006; Dahlgqvist et al., 2007; Pourret et al., 2007b; Pédrot et al., 2008; 2009), although not unambiguously with regards to the nature and source of the involved V carrier phases, as often debated elsewhere (e.g., Lyvén et al., 2003 and references therein). Key issues still have to be answered such as: which role is played by (i) the source-rock, (ii) the organic matter, (iii) the true competition between Fe- and C-based colloidal carriers for V, and whether or not the colloidal pool involved in V carriage in solution be typed.

### 4.2.1 Influence of source-rock on vanadium speciation in solution

Since the fraction of dissolved V has been shown to be primarily derived from silicates with an efficiency comparable to that of dissolved silicate during weathering, chemical weathering of silicate rocks has been considered as the primary control of the globally encountered dissolved V (Shiller and Mao, 2000; Wright and Belitz, 2010). Elbaz-Poulichet et al.

(1997) proposed that alumina-silicate colloids are a dominant host for V in water. However, V-focused studies emphasized that silicate weathering cannot be the only controlling speciation with regards to V dissolved species. The so-called ‘secondary factors’, as referred by Shiller and Mao (2000), include the nature, style and regime of the prevailing weathering processes (Gaillardet et al., 2003), redox reactions, organic-mediated complexation and anthropogenic inputs. Furthermore, Wehrli and Stumm (1989) considered that  $\text{VO}^{2+}$  has a strong tendency to coordinate with oxygen donor atoms, thus forming both strong complexes with organic chelates and becoming adsorbed especially onto hydrous oxides. Vanadium(V) - as vanadate oxyanion - behaves as phosphate and forms surface complexes with hydrous oxides by ligand exchange. These results led us to the assumption that, although not excluding a primary source of V in silicate weathering, the V stock available in wetland soil solutions mostly results from surface processes at organic matter/solution/hydrous oxide interfaces probably driven by acid-base and redox reactions. Moreover, as also stressed by Pokrovsky and Schott (2002) who did not find any relationships between V and Si in the Karelian rivers, no correlation was observed between dissolved V and Si, irrespective of the pore size cut-off used for ultrafiltration (Tables 2 and 3). Hence, dissolved V behaves independently of dissolved Si. The occurrence of large amounts of colloidal Fe and/or C that serve as efficient V carriers as assessed by the positive relationships between DOC and V as well as Fe and V (Figs. 5 and 6), as has often been previously reported, is likely to hide the fingerprint of the source-rock of V. Two studies by Dupré et al. (1999) and Pokrovsky and Schott (2002) reached the same conclusion. In the first case, these authors observed that V content and DOC decrease during successive filtrations through decreasing pore size membranes, whereas in the latter study, the dissolved V was found to be essentially associated with the Fe colloids, as their concentrations sharply decrease with decreasing pore size. The presence of high amounts of colloidal Fe or C in these rivers, which serve as a V carrier, is thus likely to hide the different silicate sources.

#### 4.2.2 Influence of the colloid type in the transport of vanadium

Since the source rocks do not reflect the major control of dissolved V speciation and considering that it is now widely admitted that colloids are major V carriers playing a significant role in both the transport and cycling of V in natural waters, the question becomes which is the prevailing nature of the colloidal carriers of V. The above discussion, with regards to the role played by the source-rocks, showed a different behaviour to that proposed by Elbaz-Poulichet et al. (1997) for the silica-rich colloids, except for very specific cases.

On one side, the observed time-linked variations showed that the onset of V in solution at the end of January and following the decline of redox potential (Fig. 2b) occurred concomitantly with the increase of DOC, Mn and Fe concentrations (Figs. 2 and 3). Nevertheless, it is not possible to assess which of the metallic or organic phases could be the most efficient V carrier. On the other side, when considering the space-linked variations, the increase of V concentrations from upland (P11) to hillslope (F5-F7), as seen in the DOC concentrations, were observed, thereby suggesting that V might be carried by C-rich phases, as also found in other studies (Wehrli and Stumm, 1989; Dupré et al., 1999; Tyler, 2004; Audry et al., 2006). This feature has already been observed for REE whose speciation is considered as being mostly organic (Gruau et al., 2004; Pourret et al., 2007b). Indeed, the largest V concentrations are observed for wetland well F14, reaching up to 12.2 mg L<sup>-1</sup> (Table 3). However, these concentrations also follow both the highest DOC and Fe contents, making it impossible to unambiguously determine whether the C- or Fe-colloids are the most efficient V carriers. Therefore, neither time-linked V nor space-linked concentration variations, in both cases positively related to the DOC and Fe variations, allowed to distinguish between the predominance of C-or Fe-colloidal carrying phases. However, Pourret et al. (2007a) suggested that the “colloidal” REE budget of samples F7 and F14 is partly controlled by REE-bearing Fe colloids and the contribution of Fe colloids estimated between ~30 and 50%.

Further information can be obtained from ultrafiltration data on hillslope and wetland samples as has been done in a previous study (Pourret et al., 2007b). The ascending hierarchical classification displayed in Figure 3 reveals - beyond the first evidence that V is mostly borne by the colloidal pool since its concentrations decrease following decreasing pore size cut-off - that the hillslope groundwater sample F7 shows a double control of V distribution by large-size (0.2  $\mu\text{m}$  and 30 kDa) Fe-rich colloids, as reported by Pédrot et al. (2009). A continuous control by a mixed DOC/Al-rich phase is also simultaneously seen, irrespective of the size of the concerned colloidal pool (Fig. 5). This control by the mixed DOC/Al-rich phase has been also already shown elsewhere, but in a similar context by Pourret et al. (2007b), who showed that concentrations of both dissolved V and Th were mostly controlled by mixed DOC/Al-rich phases, regardless of the filtration membrane cut-off. In the hillslope case, V is therefore carried on one side by the large-size ( $> 30$  kDa) Fe oxide colloidal phase and mixed DOC/Al-rich phases (Fig. 5).

Although large-size Fe colloids are also involved in V dissolved carriage, the coupled observation of Fig. 3 and Fig. 5 led to the assumption that the major colloidal control for maintaining V in dissolved phase has to be mixed DOC/Al phases since V distribution appears closer to those of DOC and Al than to that of Fe (Fig. 3). Additionally, the V versus DOC and Al distribution (Fig. 5) displays a positive relationship, regardless of the size cut-off, whereas Fe is not carried by DOC-rich low-molecular weight colloids still carrying V. This has to be compared to previous studies such as the one carried out by Pokrovsky et al. (2006), who observed that V did not exhibit any clear correlation with dissolved Fe or DOC in the  $< 0.2$   $\mu\text{m}$  fraction. By contrast, ultrafiltration performed on peat solution showed that Al played an important role as a colloidal carrier of V (Pokrovsky et al., 2005). In another context, field-flow fractionation performed on freshwaters showed that V was strongly associated to iron-rich colloids (Stolpe et al., 2005).

Another interesting point is that the observed V concentrations are also much higher than those reported for average world rivers (Johannesson et al., 2000) (Fig. 7) suggesting that the involved mixed DOC/Al colloidal carriers of V emphasize the level of dissolved V in such organic-rich environments, possibly, as proposed by Wehrli and Stumm (1989), as complexes with humic substances (HS) (Tyler, 2004) in which Al, V and HS are intimately associated. This has to be related to the fact that  $\text{VO}^{2+}$  is commonly considered as an exceptionally stable diatomic ion (Greenwood and Earnshaw, 1997), which forms strong complexes with soluble organic compounds (Aström and Corin, 2000). Such speciation information must also be linked with the sequential extraction experiments conducted on soil samples such as those of Poledniok and Buhl (2003) showing that V is mainly contained in the organic fractions.

The observation of Figure 6, corresponding to the sample recovered in the wetland (F14), led to a slightly different result, although characterized by an important combined Al/DOC control on the V distribution. In this case, the Fe distribution follows that of V throughout the pore size cuts, which was not the case for the hillslope sample (F7) which displayed a drastic fall between 0.2  $\mu\text{m}$  and 30 kDa, pointing out a non-exclusively organic speciation. Ultrafiltration data on the wetland sample (F14) point out a triple control of mixed Fe/Al/C-rich carrier phases of V, which may correspond to nano-colloidal Fe oxides embedded within Al-enriched humic substances, as elsewhere evidenced in wetlands and experimentally shown to be a significant source of bioavailable Fe (Pédrot et al., 2011). Such colloid-mediated organically complexed V is probably transported by humic substances from the source areas located in the humus-rich uppermost horizons.

Therefore, V speciation changes between the hillslope and the wetland, as assessed from the ultrafiltration data, agree with modelling calculations. Vanadium carriage moves from (i) the hillslope with a shared contribution of Fe nanooxide and organic colloids vector towards (ii) the wetland with a whole organic pool in which V, Fe and Al are complexed and embedded in organic matrices. This is also often pointed out for other trace metals elsewhere in wetlands (e.g.,



Gruau et al., 2004), whose interaction with mineral colloids is hampered by the negative charge of organic matter (i.e., Wilkinson et al., 1997), which is ubiquitous in such waterlogged environments.

## 5. Conclusions

Combining an ultrafiltration fractionation approach and modelling conducted on shallow groundwaters allowed the assessment of the main factors that control V speciation. Additionally, it can be concluded that the water samples can be divided into two groups in terms of their location along the hillslope and their associated DOC content, which are positively related to their V content (organic-rich waters recovered in wetland display the largest V concentrations). Moreover, time variations of V concentrations were also seen in wetland samples with a marked increase of V content at the winter-spring transition along with DOC, Fe and Mn content variations, as well as redox potential changes. In this context, the source rock was shown to play a minor role in V distribution, whereas the colloidal pool was shown to be the main factor controlling V speciation and its distribution in shallow groundwaters. Ascendant hierarchical classification showed that V was associated to DOC, Fe, Al, Pb, Cu, REE, U and Th, which are elements known to exhibit colloidal affinity. Speciation modelling using Model VI and SCAMP as well as ultrafiltration data evidenced a slight change in the V speciation occurring along the transect with a mixed organic-inorganic speciation in the hillslope and an organic speciation of V in the wetland probably involving Fe nanooxides embedded in Al-rich organic colloids. The binding of V in this organic environment most likely occurs through the C-rich ligand end-member, which is in agreement with the behaviour of V in shallow groundwater.

Although the role of organic matter is clearly assessed as controlling the dissolved V fraction, it appears challenging to accurately determine the real contribution of the inorganic and organic colloidal pool because the oxides are generally intimately bound to the organic matter,

621 especially in the case of organic-rich wetland soil solutions. Further study should be dedicated to  
622 clarifying this partition, notably to address the prevailing processes affecting V transport at the  
623 global scale.

624

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816 TABLE AND FIGURE CAPTIONS  
817

818 Table 1. Model VI parameters for humic substances (Tipping, 1998; Tipping, 2002).

819  
820 Table 2. SCAMP parameter values for Fe, Mn, Al and Si oxide. Site density  $\Gamma_{\max}$  is expressed in  
821  $\mu\text{mol m}^{-2}$  and P in  $\text{m}^2 \text{eq}^{-1}$  (data are from Lofts and Tipping, 1998). Values of  $\text{pK}_{\text{MH}}$  for V(IV)O  
822 are calculated from Eqns. 10 to 13 in Lofts and Tipping (1998) using well-accepted infinite-  
823 dilution (25°C) stability constants for V(IV)O first hydrolysis complexes (Peacock and Sherman,  
824 2004).

825  
826 Table 3. Physico-chemical parameters: pH, Eh (in mV) and temperature (in °C), and chemical  
827 concentrations ( $\mu\text{g L}^{-1}$ ), except for  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$  and DOC, which are reported in  $\text{mg L}^{-1}$ .

828  
829 Table 4. Ultrafiltration results; the concentrations are expressed in  $\mu\text{g L}^{-1}$ , except for  $\text{Cl}^-$ ,  $\text{NO}_3^-$   
830  $\text{SO}_4^{2-}$  and DOC which are reported in  $\text{mg L}^{-1}$ , and alkalinity in  $\mu\text{mol L}^{-1}$ .

831  
832 Table 5. Speciation results obtained using Model VI and SCAMP for groundwater from the F7  
833 and F14 wells (species proportion).

834  
835 Figure 1. Geographical location of the Petit Hermitage Catchment (France) and well water  
836 sampling placements set up along the *Le Home* toposequence.

837  
838 Figure 2. Time series results of dissolved ( $< 0.2 \mu\text{m}$ ) (a) Fe and Mn ( $\text{mg L}^{-1}$ ), (b) V and U ( $\mu\text{g L}^{-1}$ )  
839 and (c) Eh (mV) and DOC ( $\text{mg L}^{-1}$ ) content in the *Le Home* wetland samples (F14 well).

840

Figure 3. Dendograms of samples (a) F7 and (b) F14, showing the hierarchical classification of the elements in three clusters.

Figure 4. Relationships between: (a) V and DOC and (b) V and Fe concentrations for the F14 groundwater samples. The data are expressed in  $\text{mg L}^{-1}$  except for V ( $\mu\text{g L}^{-1}$ ). The corresponding values are provided in Table 3.

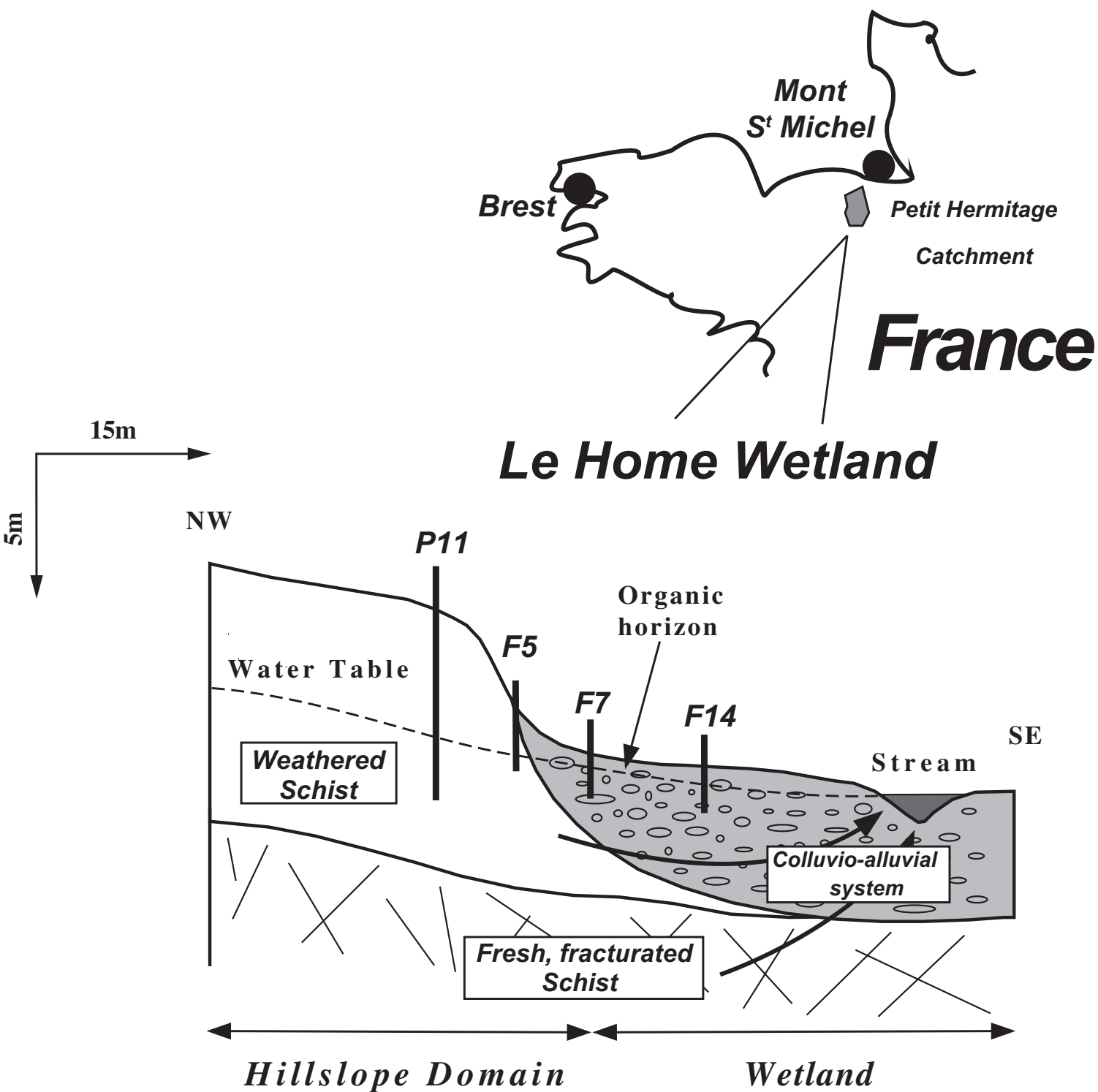
Figure 5. Variations of (a) V and Al versus DOC concentrations and (b) V and Fe versus DOC concentrations in the different filtrates for the F7 well. The corresponding values are provided in Table 4.

Figure 6. Variations of (a) V and Al versus DOC concentrations and (b) V and Fe versus DOC concentrations in the different filtrates for the F14 well. The corresponding values are provided in Table 4.

Figure 7. Eh/pH diagram for inorganic V species at  $25^{\circ}\text{C}$  and 1 atm for a V concentration of  $10 \mu\text{mol L}^{-1}$  (Breit and Wanty, 1991; Peacock and Sherman, 2004; Templeton and Chasteen, 1980; Wanty and Goldhaber, 1992; Wehrli and Stumm, 1989). Vanadium data (black dots) are from Table 2.



Figure 1



**Figure 2**

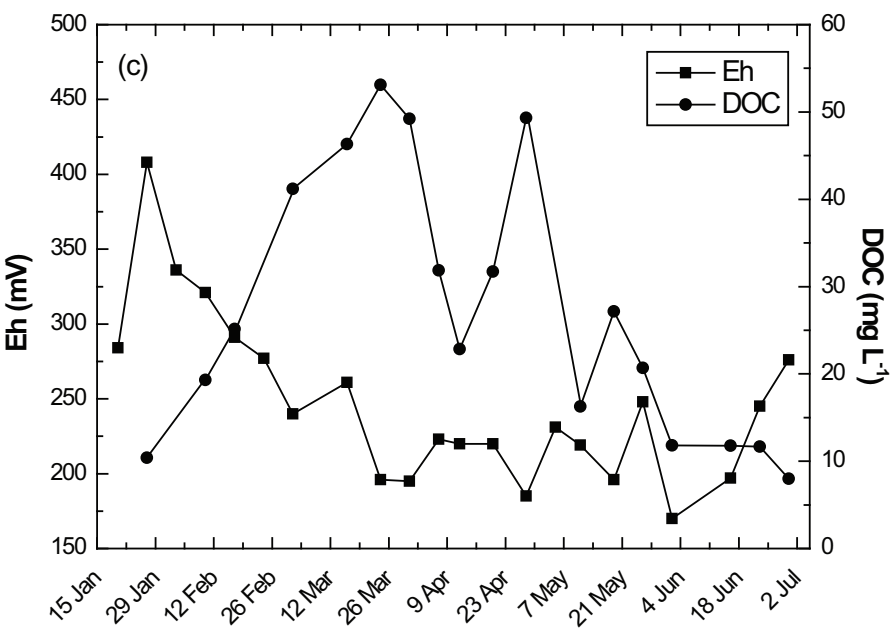
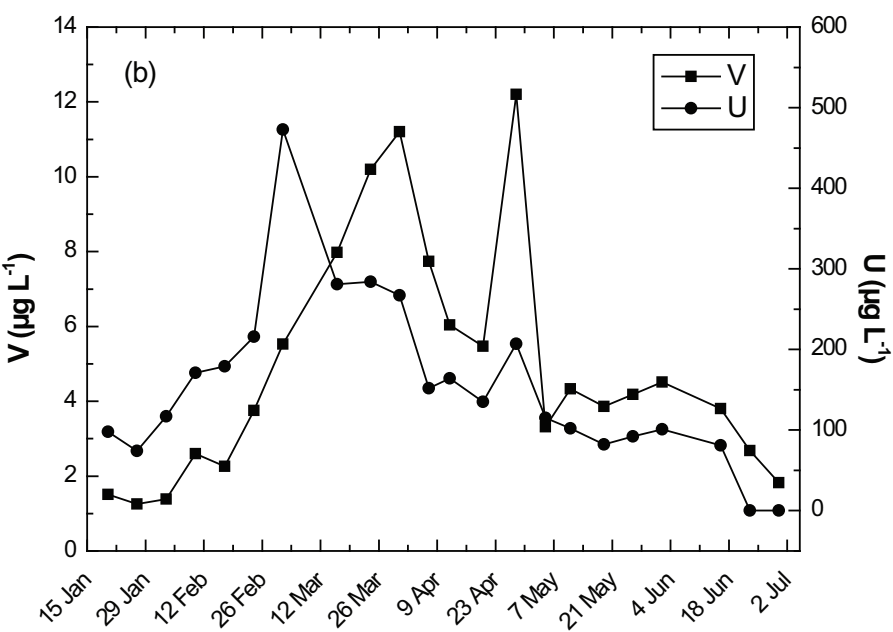
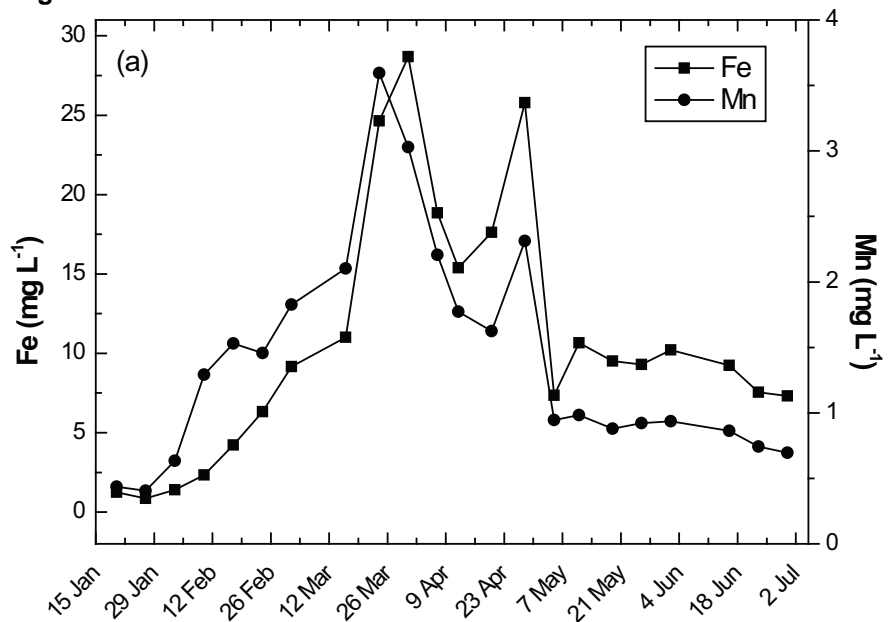
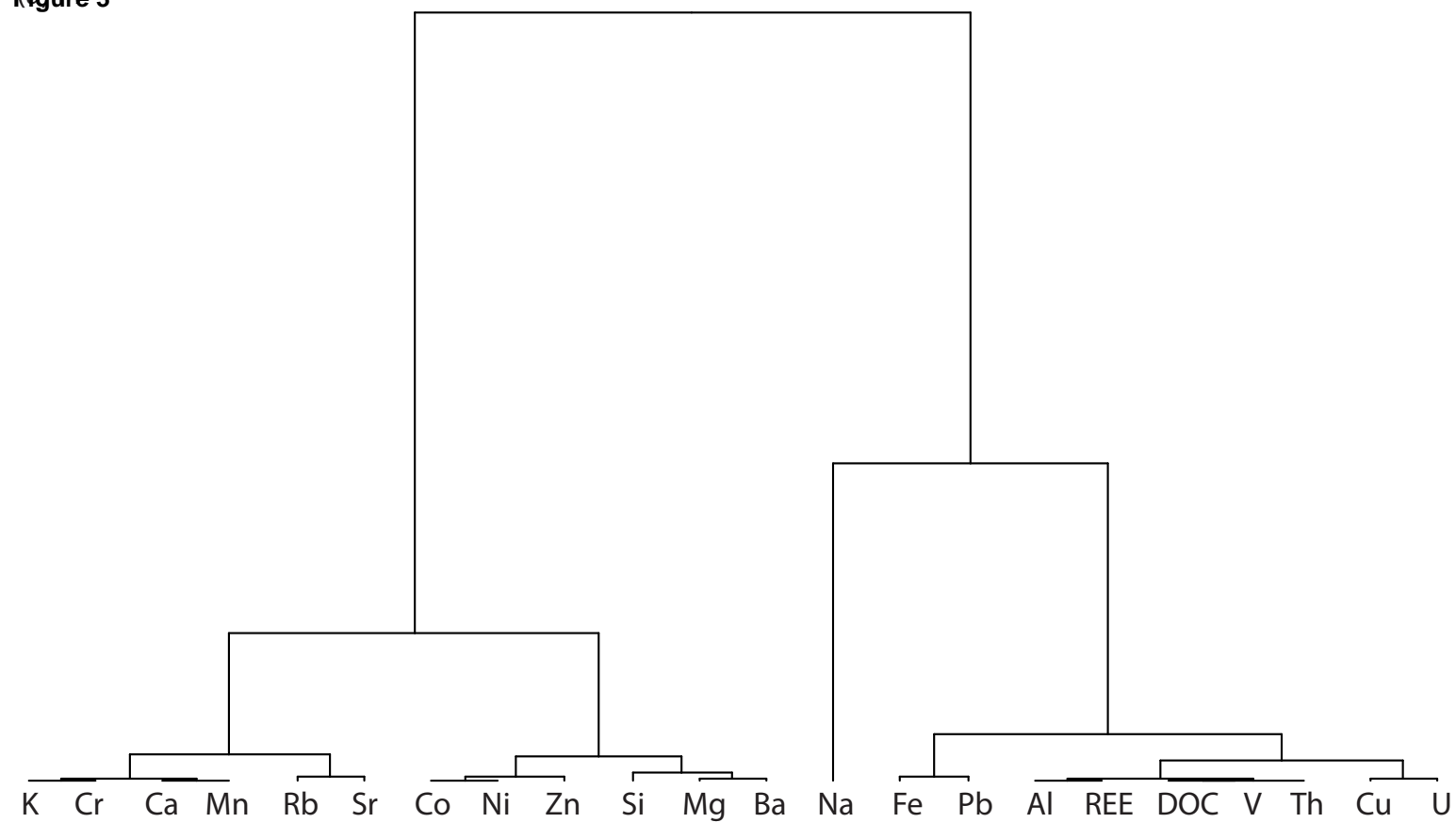


Figure 3



(b) F14

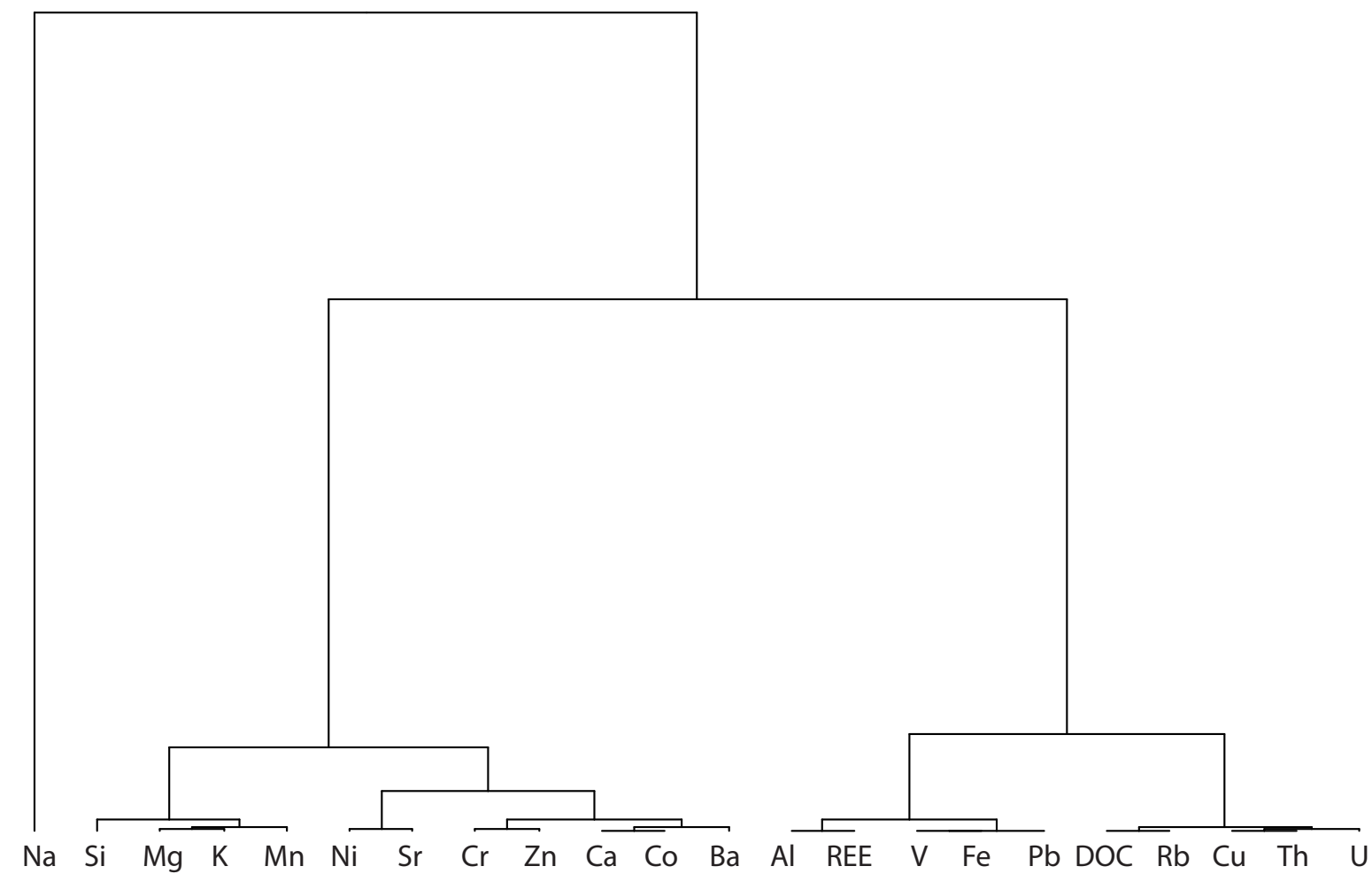


Figure 4

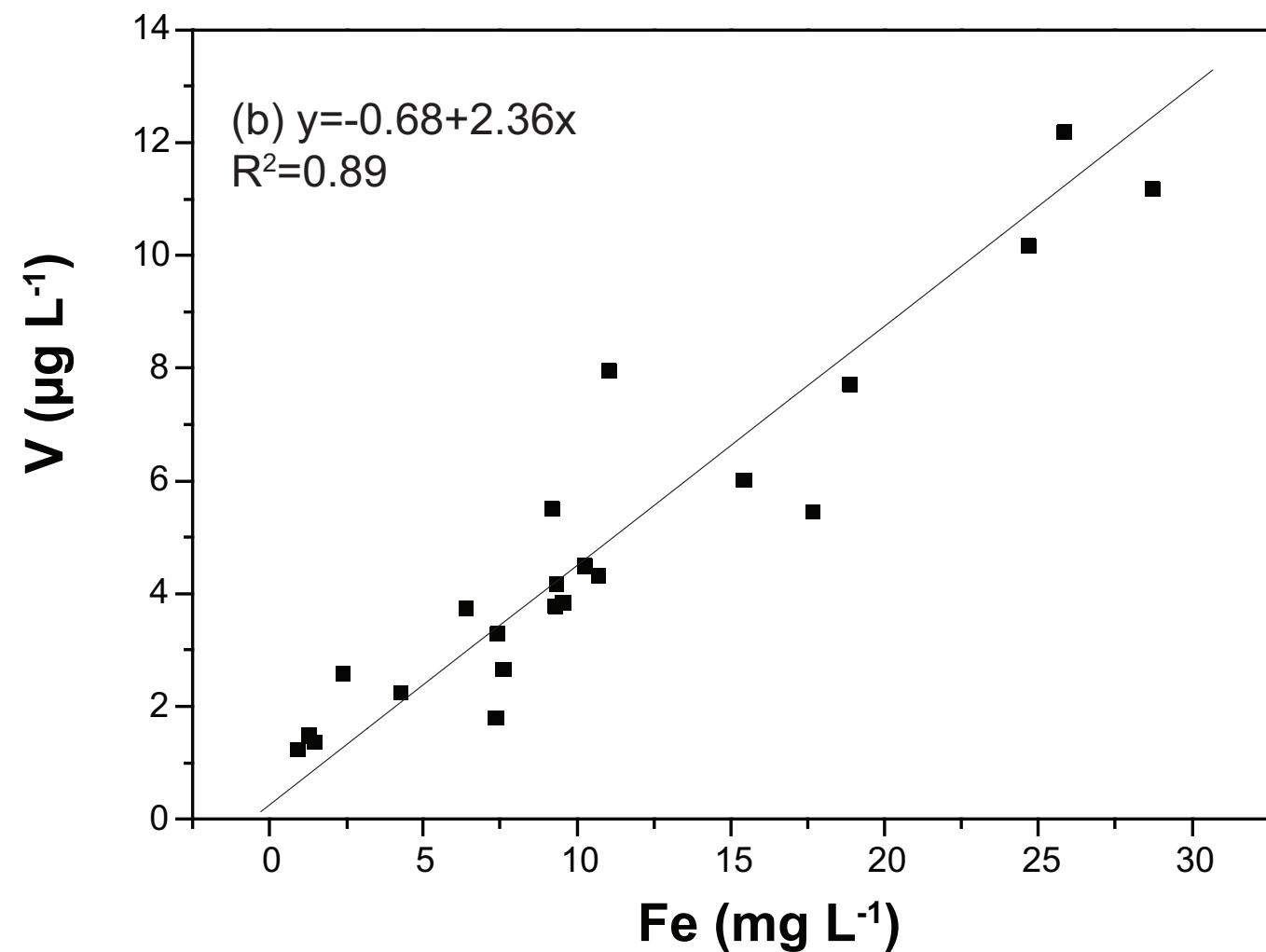
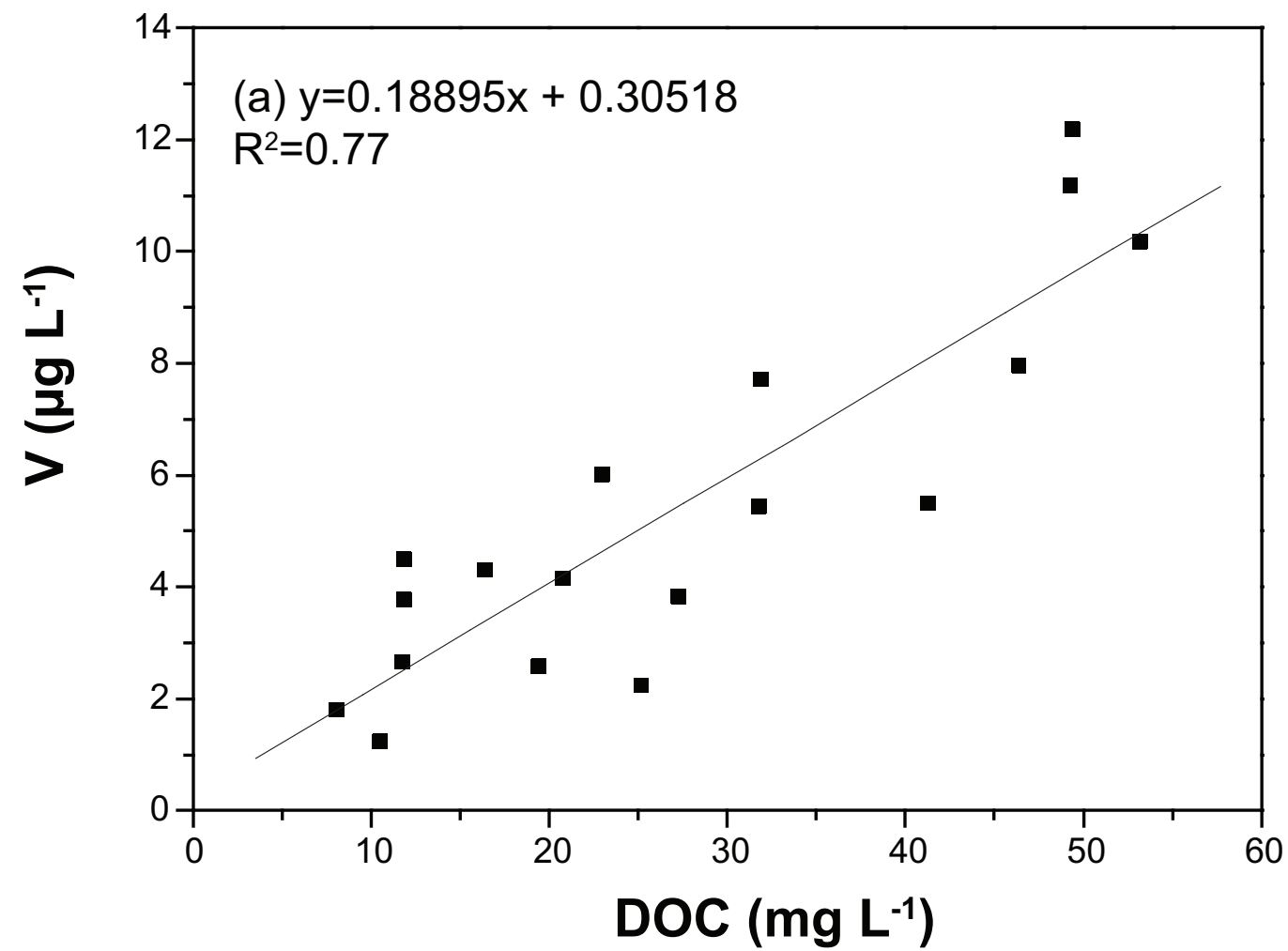


Figure 5

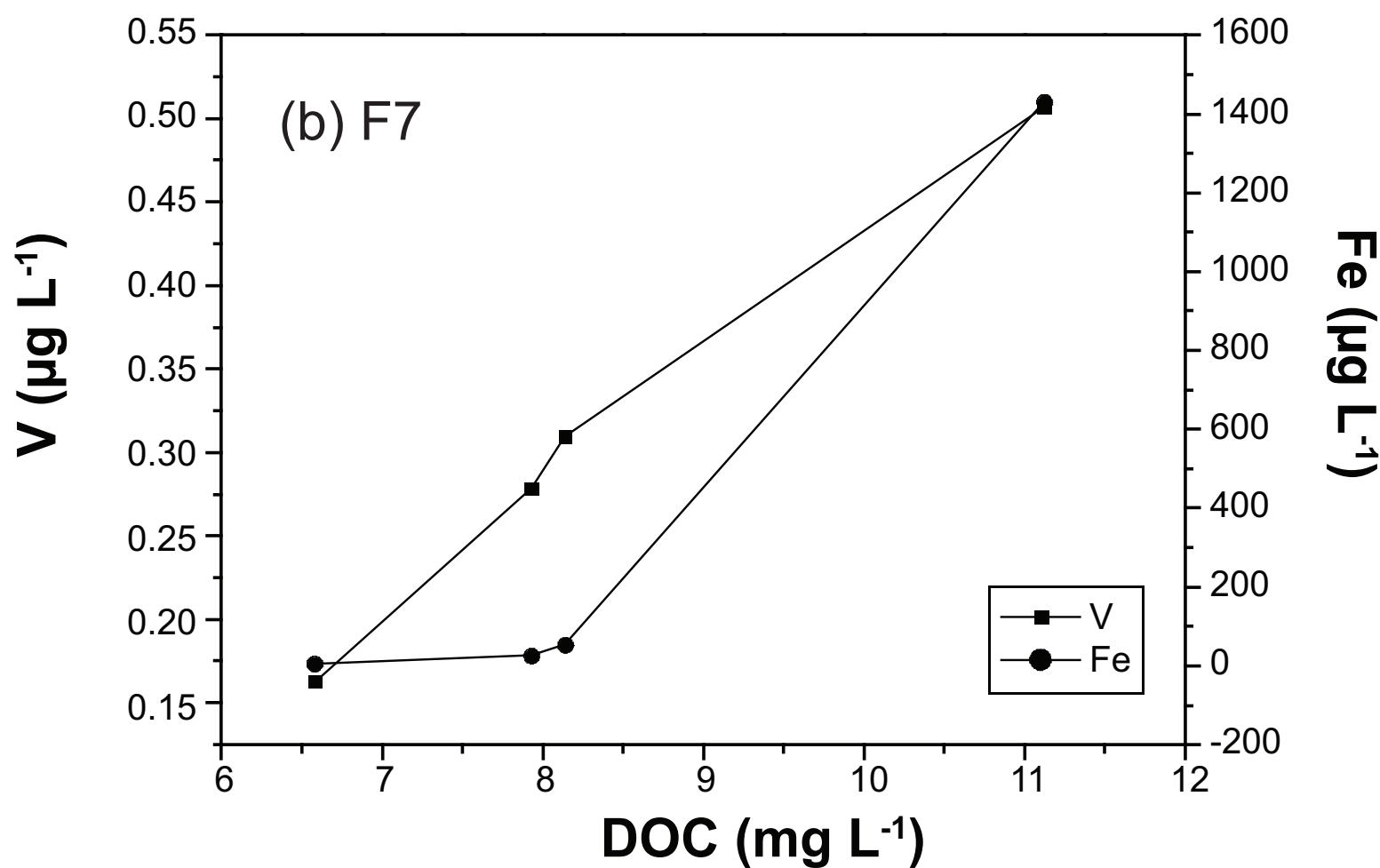
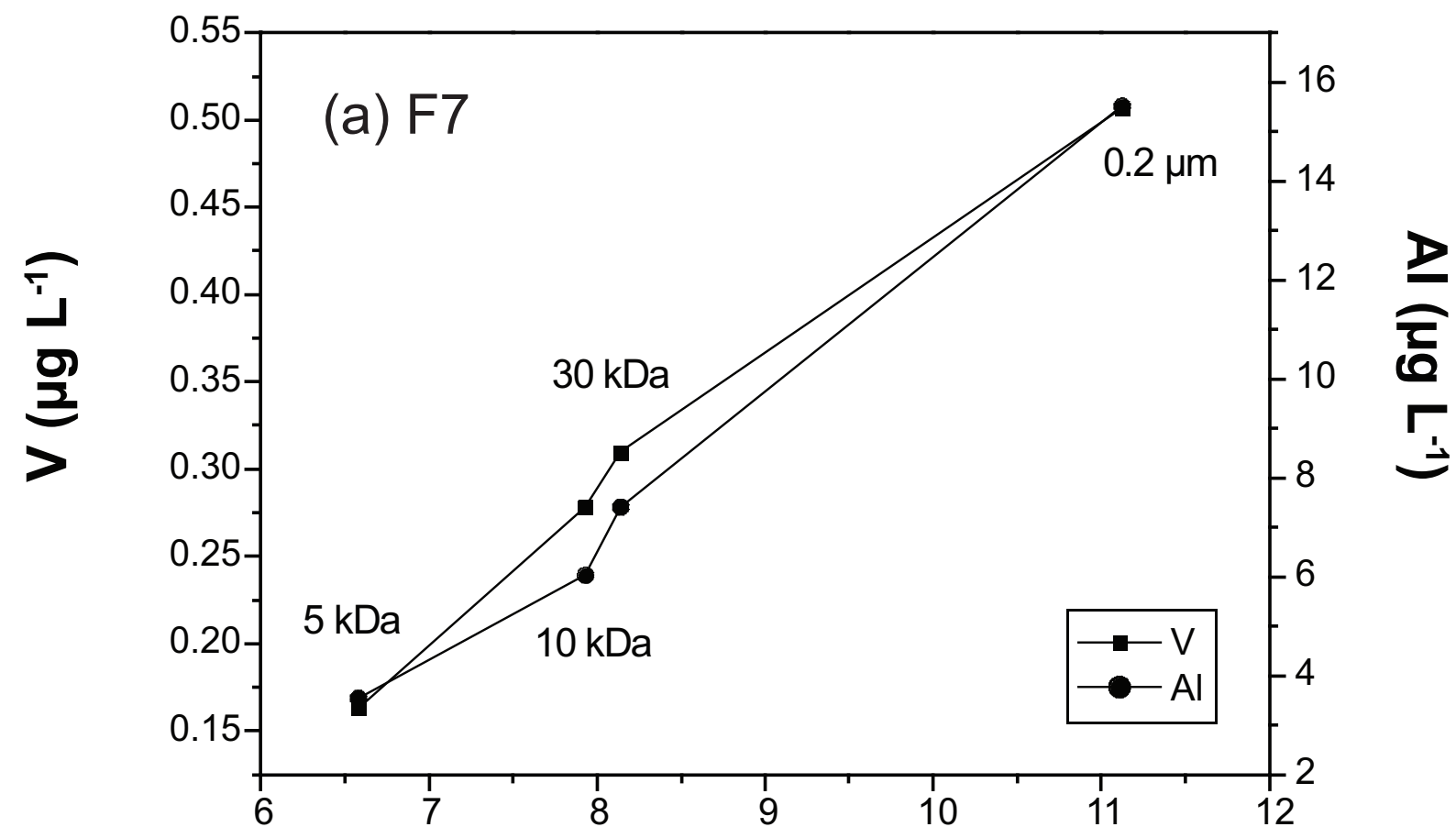
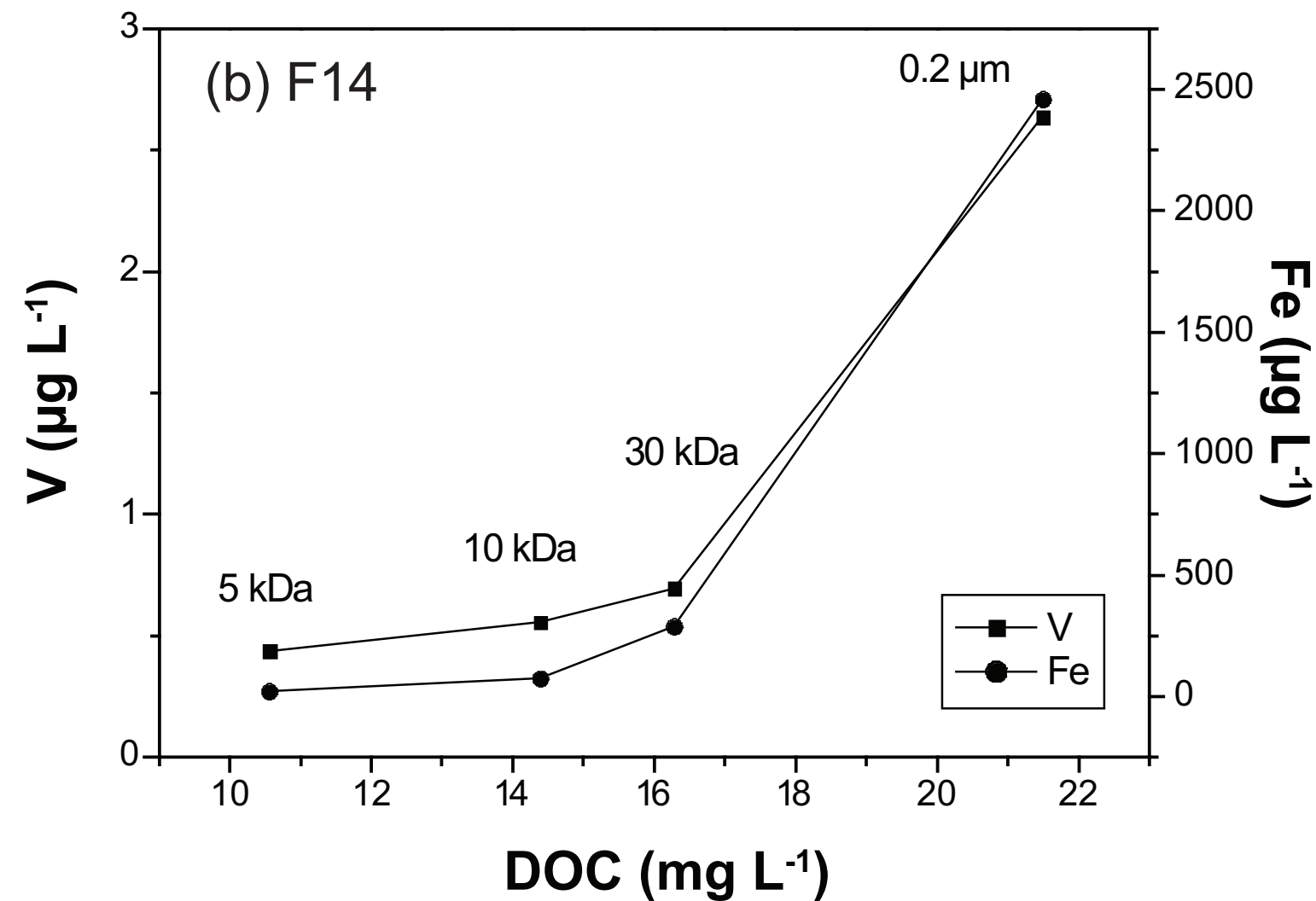
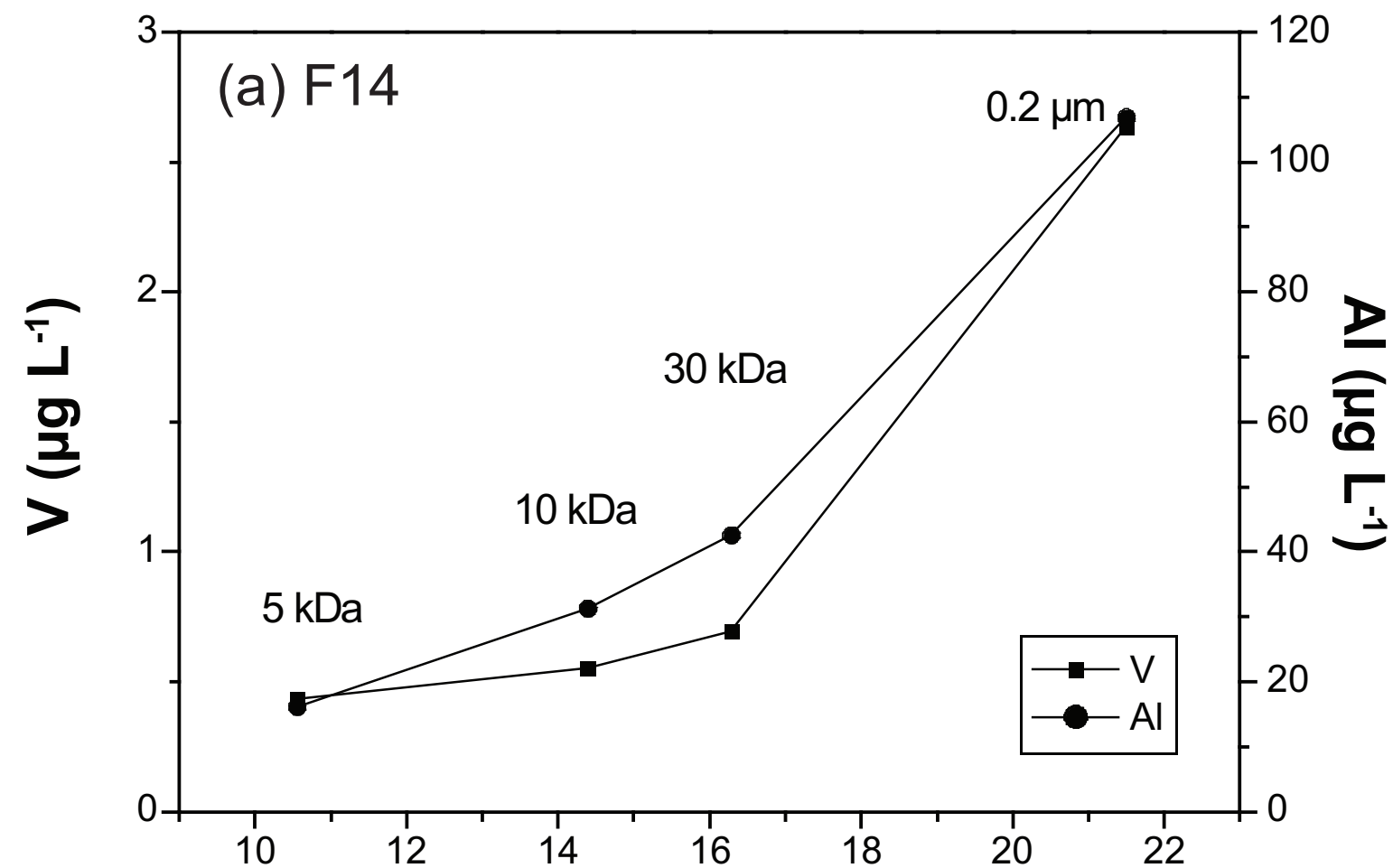
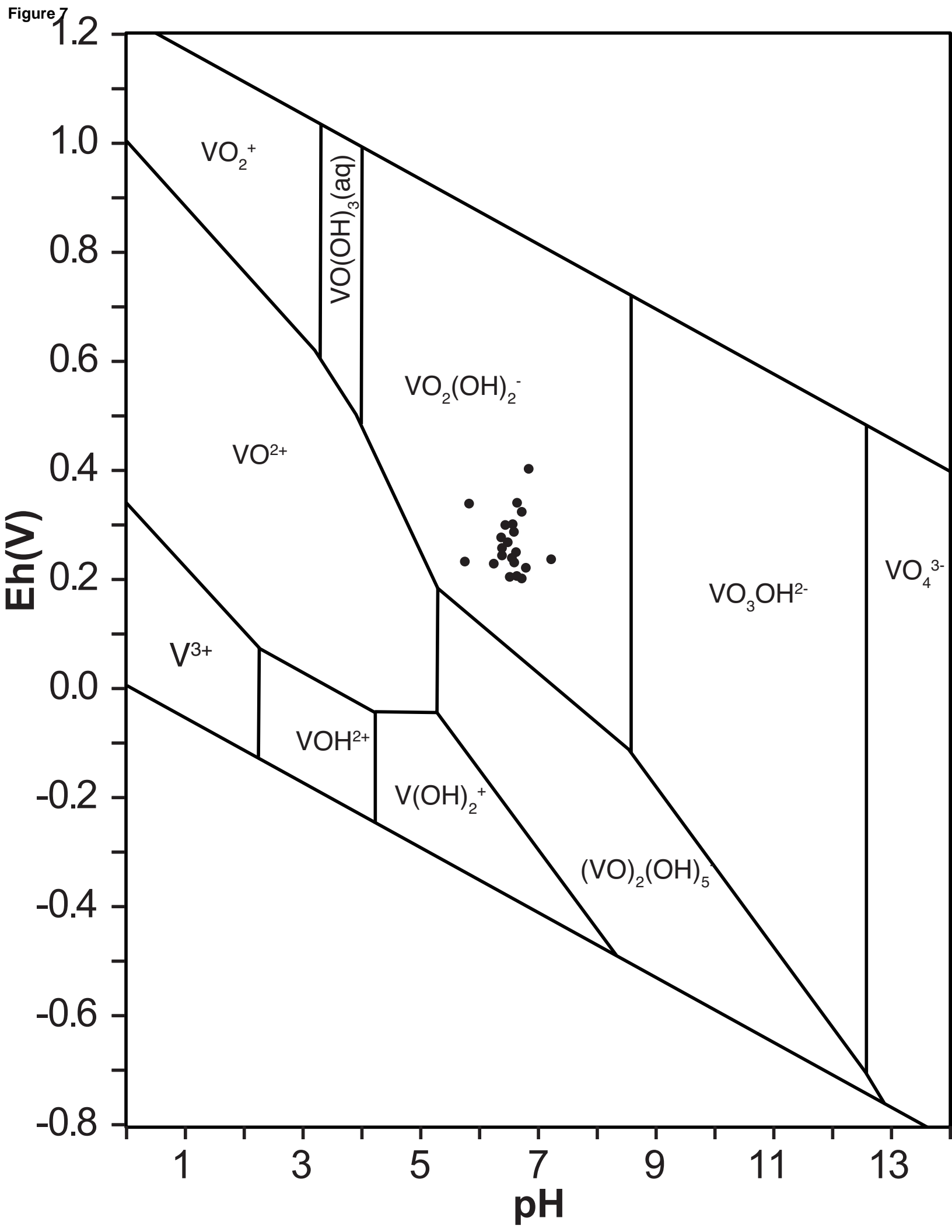


Figure 6





| Parameter     | Description  | Values   |
|---------------|--|--|
| $n_A$         | Amount of type-A sites ( $\text{mol g}^{-1}$ )                                 | $4.8 \times 10^{-3}$ (FA), $3.3 \times 10^{-3}$ (HA) |
| $n_B$         | Amount of type-B sites ( $\text{mol g}^{-1}$ )                                 | $0.5 \times n_A$                                     |
| $pK_A$        | Intrinsic proton dissociation constant for type-A sites                        | 3.2 (FA), 4.1 (HA)                                   |
| $pK_B$        | Intrinsic proton dissociation constant for type-B sites                        | 9.4 (FA), 8.8 (HA)                                   |
| $\Delta pK_A$ | Distribution term that modifies $pK_A$   | 3.3 (FA), 2.1 (HA)                                   |
| $\Delta pK_B$ | Distribution term that modifies $pK_B$   | 4.9 (FA), 3.6 (HA)                                   |
| $\log K_{MA}$ | Intrinsic equilibrium constant for metal binding at type-A sites               | 2.4 (FA), 2.5 (HA)                                   |
| $\log K_{MB}$ | Intrinsic equilibrium constant for metal binding at type-B sites               | $3.39 \log K_{MA} - 1.15$                            |
| $\Delta LK_1$ | Distribution term that modifies $\log K_{MA}$                                  | 2.8  |
| $\Delta LK_2$ | Distribution term that modifies the strength of bidentate and tridentate sites | 1.74 (V(IV)O)  |
| P             | Electrostatic parameter  | -115 (FA), -330 (HA)                                 |
| $K_{sel}$     | Selectivity coefficient for counterion accumulation                            | 1  |
| $f_{prB}$     | Fraction of proton sites that can form bidentate sites                         | Calculated from geometry                             |
| $f_{prT}$     | Fraction of proton sites that can form tridentate sites                        | Calculated from geometry                             |
| M             | Molecular weight   | 1.5 kDa (FA), 15 kDa (HA)                            |
| R             | Molecular radius   | 0.8 nm (FA), 1.72 nm (HA)                            |

**Table 1.**



|                                | AlOx  | FeOx  | MnOx  | SiOx  |
|--------------------------------|-------|-------|-------|-------|
| $\Gamma_{\max}$                | 8.33  | 8.33  | 8.33  | 8.33  |
| $\text{pK}_{\text{H1}}$        | 6.45  | 6.26  | 0.63  | (-10) |
| $\text{pK}_{\text{H2}}$        | 9.96  | 9.66  | 4.21  | 8.51  |
| $10^6 \text{ P}$               | -1.38 | -1.46 | -0.88 | -0.86 |
| $\Delta \text{pK}_{\text{MH}}$ | -2.2  | -2    | -3    | -1.5  |
| $\text{pK}_{\text{MH}}$        | 2.4   | 2.7   | 1.1   | 4.7   |

**Table 2.**

|                 | P11      | F5       | F5       | F7       | F7       | F14      |          |          |          |          |          |          |          |          |
|-----------------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|
| Date            | 01/20/99 | 02/26/98 | 01/20/99 | 02/26/98 | 01/20/99 | 01/20/99 | 01/27/99 | 02/03/99 | 02/10/99 | 02/17/99 | 02/24/99 | 03/03/99 | 03/16/99 | 03/24/99 |
| T (°C)          | 11.1     | n.a.     | 10.9     | n.a.     | 12.7     | 9.4      | 8.1      | 7.6      | 7.0      | 7.6      | 9.1      | 10.1     | 10.1     | 11.5     |
| pH              | 5.95     | n.a.     | 6.05     | n.a.     | 6.07     | 5.6      | 6.59     | 6.4      | 6.46     | 6.31     | 6.33     | 6.36     | 6.95     | 6.45     |
| Eh              | 405      | n.a.     | 420      | n.a.     | 348      | 284      | 408      | 336      | 321      | 291      | 277      | 240      | 261      | 196      |
| Cl              | 43.16    | n.a.     | 49.46    | n.a.     | 47.3     | 36.32    | 33.84    | 34.67    | 34.98    | 35.79    | 34.78    | 34.05    | 36.91    | 37.84    |
| SO <sub>4</sub> | 17.31    | n.a.     | 23.61    | n.a.     | 25.46    | 18.08    | 16.03    | 18.54    | 14.02    | 16.4     | 15.8     | 13.78    | 4.66     | 11       |
| NO <sub>3</sub> | 67.42    | n.a.     | 69.71    | n.a.     | 46.27    | 15.47    | 19.29    | 41.88    | 6.84     | 14.39    | 16.05    | 0        | 0        | 11.41    |
| DOC             | n.a.     | 4.4      | n.a.     | 3.9      | n.a.     | n.a.     | 10.409   | n.a.     | 19.313   | 25.136   | n.a.     | 41.19    | 46.31    | 53.12    |
| Na              | 26290    | n.a.     | 22370    | n.a.     | 20080    | 19680    | 18400    | 18430    | 19040    | 19480    | 18680    | 18820    | 19150    | 19490    |
| Mg              | 10440    | n.a.     | 14140    | n.a.     | 12060    | 7033     | 6283     | 7715     | 7538     | 8376     | 7901     | 9907     | 10380    | 10710    |
| Al              | 4        | 2        | 4        | 7        | 5        | 109      | 92       | 89       | 157      | 129      | 131      | 151      | 188      | 170      |
| Si              | 8980     | 699      | 7770     | 808      | 7293     | 8477     | 7853     | 10340    | 8870     | 9298     | 9177     | 11560    | 7056     | 12480    |
| K               | 1700     | n.a.     | 4428     | n.a.     | 2595     | 2502     | 2766     | 1522     | 2114     | 1761     | 1677     | 1225     | 1755     | 1644     |
| Ca              | 15080    | n.a.     | 21150    | n.a.     | 18650    | 14310    | 12820    | 18250    | 17320    | 20050    | 19970    | 24240    | 21650    | 37610    |
| V               | 0.32     | 0.78     | 0.37     | 1.42     | 0.95     | 1.51     | 1.25     | 1.39     | 2.60     | 2.26     | 3.75     | 5.53     | 7.98     | 10.22    |
| Cr              | 2.01     | 4.00     | 1.95     | 2.40     | 0.70     | 1.43     | 1.37     | 1.49     | 1.86     | 1.62     | 1.62     | 2.01     | 2.86     | 2.43     |
| Mn              | 29       | 9        | 12       | 94       | 65       | 437      | 405      | 633      | 1292     | 1530     | 1456     | 1826     | 2102     | 3595     |
| Fe              | 91       | 93       | 307      | 168      | 373      | 1246     | 853      | 1408     | 2339     | 4220     | 6329     | 9160     | 11000    | 24640    |
| Co              | 0.10     | 0.23     | 0.19     | 0.88     | 0.56     | 2.63     | 2.05     | 2.92     | 7.41     | 8.06     | 8.47     | 10.10    | 11.36    | 14.38    |
| Ni              | 3.42     | 2.40     | 2.45     | 2.08     | 2.29     | 6.16     | 5.26     | 7.00     | 10.46    | 10.16    | 10.18    | 11.74    | 13.62    | 15.84    |
| Cu              | 0.94     | 0.40     | 0.96     | 1.11     | 1.17     | 4.61     | 3.31     | 4.21     | 6.24     | 5.29     | 4.64     | 4.71     | 4.38     | 2.31     |
| Zn              | 2.76     | 4.10     | 11.98    | 6.00     | 8.00     | 7.19     | 7.60     | 8.17     | 10.70    | 9.44     | 8.02     | 11.76    | 9.61     | 8.81     |
| Rb              | n.a.     | 1.13     | n.a.     | 1.38     | n.a.     | n.a.     | n.a.     | n.a.     | n.a.     | n.a.     | n.a.     | n.a.     | n.a.     | n.a.     |
| Sr              | 138      | 191      | 190      | 149      | 172      | 133      | 117      | 174      | 155      | 179      | 176      | 222      | 192      | 235      |
| Ba              | 28       | 30       | 31       | 36       | 41       | 28       | 26       | 30       | 31       | 33       | 33       | 37       | 35       | 41       |
| ΣREE            | 0.176    | 0.253    | 0.292    | 0.624    | 0.510    | 6.805    | 4.794    | 6.720    | 11.713   | 10.416   | 11.709   | 15.261   | 16.486   | 15.821   |
| Pb              | 0.617    | 10.050   | 18.750   | 1.555    | 2.980    | 6.320    | 5.220    | 5.160    | 7.690    | 7.280    | 6.540    | 9.120    | 14.180   | 8.900    |
| Th              | 0.110    | 0.011    | 0.135    | 0.038    | 0.230    | 1.850    | 1.400    | 1.680    | 3.180    | 2.760    | 2.740    | 4.280    | 5.340    | 4.950    |
| U               | 0.104    | 0.069    | 0.119    | 0.115    | 0.066    | 0.983    | 0.742    | 1.170    | 1.710    | 1.790    | 2.160    | 4.730    | 2.810    | 2.840    |

**Table 3.** (to be continued)

n.a.: not available

|                 | F14      |          |          |          |          |          |          |          |          |          |          |          |          |
|-----------------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|
| Date            | 03/31/99 | 04/07/99 | 04/12/99 | 04/20/99 | 04/28/99 | 05/05/99 | 05/11/99 | 05/19/99 | 05/26/99 | 06/02/99 | 06/16/99 | 06/23/99 | 06/30/99 |
| T (°C)          | 12.6     | 11.9     | 10.4     | 11.4     | 13.7     | 14.2     | 13.8     | 13.2     | 16.6     | 13.2     | 17.3     | 18.8     | 16.4     |
| pH              | 6.38     | 6.31     | 6.35     | 6.54     | 6.27     | 6.14     | 6.14     | 6        | 6.15     | 5.53     | n.d.     | 6.23     | 6.21     |
| Eh              | 195      | 223      | 220      | 220      | 185      | 231      | 219      | 196      | 248      | 170      | 197      | 245      | 276      |
| Cl              | 39.3     | 35.83    | 34.83    | 34.98    | 29.55    | 33.57    | 34.8     | 34.41    | 32.26    | 32.99    | 32.59    | 31.95    | 31.57    |
| SO <sub>4</sub> | 14.05    | 16.76    | 16.71    | 13.56    | 7.56     | 20.2     | 19.21    | 18.74    | 18.23    | 18.04    | 17.29    | 18.93    | 23.5     |
| NO <sub>3</sub> | 9.14     | 8.07     | 0        | 33.56    | 15.6     | n.a.     | 4.84     | 2.07     | 3.84     | 2.64     | 3.52     | 8.72     | 23.66    |
| DOC             | 49.21    | 31.84    | 22.85    | 31.72    | 49.31    | n.a.     | 16.27    | 27.17    | 20.7     | 11.8     | 11.76    | 11.65    | 7.98     |
| Na ppb          | 19750    | 19390    | 19560    | 16860    | 18200    | 18740    | 18130    | 18130    | 18080    | 18640    | 17833    | 17330    | 17030    |
| Mg              | 9765     | 8406     | 8300     | 7432     | 7846     | 7559     | 6922     | 6754     | 6902     | 7115     | 6875     | 7094     | 6233     |
| Al              | 165      | 106      | 95       | 109      | 165      | 45       | 69       | 66       | 69       | 63       | 60       | 48       | 42       |
| Si              | 12890    | 12940    | 13670    | 12700    | 9888     | 14870    | 14210    | 13710    | 13630    | 14150    | 13080    | 16760    | 15640    |
| K               | 1709     | 1181     | 1123     | 1391     | 1460     | 575      | 667      | 658      | 475      | 489      | 464      | 497.7    | 516.5    |
| Ca              | 34100    | 33630    | 32660    | 26850    | 32440    | 26560    | 24400    | 22160    | 23440    | 24220    | 22805    | 23280    | 21660    |
| V               | 11.22    | 7.74     | 6.04     | 5.47     | 12.21    | 3.32     | 4.33     | 3.86     | 4.18     | 4.51     | 3.80     | 2.68     | 1.83     |
| Cr              | 2.39     | 1.86     | 1.54     | 1.65     | 2.89     | 0.79     | 1.17     | 1.18     | 1.13     | 1.11     | 1.05     | 0.90     | 0.75     |
| Mn              | 3028     | 2206     | 1773     | 1625     | 2312     | 945      | 982      | 880      | 921      | 935      | 863      | 742      | 695      |
| Fe              | 28680    | 18840    | 15380    | 17630    | 25780    | 7355     | 10660    | 9511     | 9297     | 10220    | 9231     | 7550     | 7307     |
| Co              | 13.74    | 9.71     | 7.68     | 8.45     | 11.58    | 3.92     | 5.29     | 4.95     | 5.36     | 5.27     | 4.95     | 4.32     | 4.47     |
| Ni              | 12.05    | 9.73     | 7.87     | 8.09     | 11.73    | 5.46     | 6.55     | 6.40     | 7.00     | 6.72     | 6.41     | 5.83     | 5.46     |
| Cu              | 1.90     | 1.40     | 1.32     | 1.15     | 1.95     | 0.63     | 0.87     | 0.98     | 0.89     | 0.80     | 0.83     | 0.76     | 1.12     |
| Zn              | 8.13     | 7.26     | 5.98     | 6.32     | 19.33    | 4.60     | 3.99     | 4.07     | 4.23     | 3.59     | 3.84     | 3.53     | 6.99     |
| Rb              | n.a.     | 0.92     | 0.88     | 0.90     | 1.00     | 0.53     | 0.57     | 0.59     | 0.48     | 0.52     | 0.44     | 0.43     | 0.55     |
| Sr              | 223      | 198      | 198      | 167      | 195      | 163      | 153      | 140      | 148      | 157      | 148      | 143      | 136      |
| Ba              | 41       | 34       | 34       | 33       | 34       | 31       | 29       | 27       | 29       | 29       | 27       | 26       | 27       |
| ΣREE            | 15.655   | 10.514   | 9.255    | n.a.     | 15.479   | 6.921    | 8.373    | 6.791    | 7.854    | 8.132    | 6.744    | 5.633    | 4.406    |
| Pb              | 8.750    | 5.310    | 4.590    | 7.340    | 11.480   | 2.260    | 3.710    | 3.600    | 3.480    | 2.880    | 2.682    | 0.002    | 0.002    |
| Th              | 5.000    | 2.200    | 1.890    | 2.390    | 3.930    | 1.010    | 1.520    | 1.230    | 1.330    | 1.320    | 1.190    | 1.100    | 0.771    |
| U               | 2.670    | 1.520    | 1.640    | 1.350    | 2.070    | 1.150    | 1.020    | 0.823    | 0.922    | 1.010    | 0.811    | 0.001    | 0.001    |

**Table 3.**

n.a.: not available

|                 | F7          |        |        |        |        |        |        | F14         |        |        |        |        |        |        |
|-----------------|-------------|--------|--------|--------|--------|--------|--------|-------------|--------|--------|--------|--------|--------|--------|
|                 | 0.2 $\mu$ m | 30 kDa | 30 kDa | 10 kDa | 10 kDa | 5 kDa  | 5 kDa  | 0.2 $\mu$ m | 30 kDa | 30 kDa | 10 kDa | 10 kDa | 5 kDa  | 5 kDa  |
| T (°C)          | 10.6        |        |        |        |        |        |        | 10.4        |        |        |        |        |        |        |
| pH              | 6.19        |        |        |        |        |        |        | 6.40        |        |        |        |        |        |        |
| Cl              | 69          |        |        |        |        |        |        | 53          |        |        |        |        |        |        |
| SO <sub>4</sub> | 62          |        |        |        |        |        |        | 35          |        |        |        |        |        |        |
| NO <sub>3</sub> | 1           |        |        |        |        |        |        | 1           |        |        |        |        |        |        |
| Alkalinity      | 1.318       |        |        |        |        |        |        | 623         |        |        |        |        |        |        |
| DOC             | 11.1        | 8.2    | 8.1    | 8.0    | 7.8    | 6.9    | 6.3    | 21.5        | 16.3   | 16.2   | 14.7   | 14.1   | 10.6   | 10.5   |
| Na              | 35,090      | 40,830 | 40,830 | 35,410 | 35,410 | 37,650 | 37,650 | 24,000      | 22,260 | 24,810 | 24,760 | 24,030 | 19,882 | 19,494 |
| Mg              | 12,150      | 12,780 | 13,000 | 15,680 | 11,450 | 12,160 | 11,510 | 7,613       | 6,738  | 7,460  | 7,332  | 7,297  | 6,222  | 6,064  |
| Al              | 16          | 10     | 9      | 9      | 7      | 8      | 5      | 107         | 41     | 44     | 33     | 30     | 16     | 16     |
| Si              | 14,220      | 15,050 | 15,730 | 18,420 | 13,860 | 14,740 | 13,740 | 12,860      | 11,610 | 13,190 | 13,110 | 12,705 | 11,674 | 11,294 |
| K               | 463         | 477    | 531    | 603    | 463    | 445    | 405    | 895         | 845    | 895    | 902    | 873    | 809    | 772    |
| Ca              | 30,800      | 32,270 | 34,840 | 40,370 | 30,850 | 31,600 | 29,570 | 24,880      | 23,220 | 24,730 | 24,290 | 23,648 | 22,389 | 21,481 |
| V               | 0.51        | 0.29   | 0.32   | 0.37   | 0.28   | 0.35   | 0.25   | 2.64        | 0.68   | 0.72   | 0.57   | 0.55   | 0.46   | 0.42   |
| Cr              | 0.91        | 1.07   | 1.20   | 1.35   | 1.03   | 0.95   | 0.82   | 1.71        | 1.44   | 1.51   | 1.32   | 1.22   | 0.83   | 0.73   |
| Mn              | 1,193       | 1,239  | 1,316  | 1,572  | 1,178  | 1,206  | 1,135  | 512         | 417    | 436    | 430    | 418    | 13     | 13     |
| Fe              | 1.431       | 373    | 372    | 46     | 51     | 30     | 22     | 2,462       | 275    | 305    | 83     | 69     | 20     | 26     |
| Co              | 6.72        | 6.84   | 7.34   | 8.20   | 6.22   | 6.15   | 5.51   | 4.74        | 3.46   | 3.72   | 3.46   | 3.31   | 0.14   | 0.14   |
| Ni              | 11.72       | 11.79  | 12.67  | 13.81  | 10.46  | 9.62   | 7.98   | 11.71       | 9.54   | 14.54  | 10.97  | 8.93   | 6.53   | 6.60   |
| Cu              | 2.52        | 2.29   | 2.43   | 2.39   | 1.83   | 1.87   | 1.38   | 10.19       | 7.42   | 7.90   | 6.51   | 5.69   | 4.73   | 4.50   |
| Zn              | 8.43        | 7.45   | 8.62   | 9.55   | 7.41   | 7.60   | 6.60   | 12.41       | 10.99  | 9.27   | 9.26   | 8.41   | 5.72   | 5.31   |
| Rb              | 1.72        | 1.76   | 1.92   | 2.28   | 1.75   | 1.72   | 1.60   | 0.88        | 0.86   | 0.88   | 0.88   | 0.85   | 0.87   | 0.85   |
| Sr              | 189.60      | 195.80 | 212.30 | 259.30 | 193.70 | 196.90 | 184.90 | 155.10      | 149.50 | 159.90 | 152.60 | 148.21 | 144.53 | 143.03 |
| Ba              | 51.20       | 51.38  | 56.42  | 66.37  | 51.62  | 49.76  | 46.72  | 34.21       | 29.95  | 29.75  | 29.42  | 28.83  | 22.39  | 21.81  |
| ΣREE            | 3.793       | 1.539  | 1.796  | 1.625  | 1.220  | 1.407  | 0.663  | 8.649       | 2.777  | 2.778  | 1.746  | 1.557  | 0.651  | 0.656  |
| Pb              | 0.057       | 0.031  | 0.006  | 0.002  | 0.031  | 0.027  | 0.026  | 1.195       | 0.096  | 0.085  | 0.011  | 0.013  | 0.023  | 0.018  |
| Th              | 0.037       | 0.019  | 0.019  | 0.015  | 0.011  | 0.007  | 0.003  | 0.163       | 0.098  | 0.099  | 0.060  | 0.049  | 0.013  | 0.013  |
| U               | 0.061       | 0.049  | 0.051  | 0.051  | 0.039  | 0.038  | 0.029  | 0.118       | 0.067  | 0.065  | 0.045  | 0.039  | 0.017  | 0.017  |

**Table 4.**

|     | <i>HA</i> | <i>FA</i> | <i>Inorganic</i> |
|-----|-----------|-----------|------------------|
| F7  | 47        | 47        | 6                |
| F14 | 58        | 41        | 1                |

**Table 5.**