



**HAL**  
open science

## Natural suspended particulate matter (SPM) versus lab-controlled particles: Comparison of the reactivity and association mode of Zn

Mathieu Le Meur, Emmanuelle Montargès-Pelletier, Renaud Gley, Valérie Briois, Laurent Michot, Hussein Kanbar, Céline Caillet, Angelina Razafitianamaharavo, Frédéric Villieras

### ► To cite this version:

Mathieu Le Meur, Emmanuelle Montargès-Pelletier, Renaud Gley, Valérie Briois, Laurent Michot, et al.. Natural suspended particulate matter (SPM) versus lab-controlled particles: Comparison of the reactivity and association mode of Zn. *Applied Geochemistry*, 2022, pp.105286. 10.1016/j.apgeochem.2022.105286 . hal-03627844

HAL Id: hal-03627844

<https://hal.univ-lorraine.fr/hal-03627844v1>

Submitted on 20 Nov 2022

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Distributed under a Creative Commons Attribution - NonCommercial - NoDerivatives 4.0 International License

1           **Natural Suspended Particulate Matter (SPM) versus lab controlled**  
2           **particles: comparison of reactivity and association mode of Zn.**

3           Mathieu LE MEUR<sup>1,2</sup>, Emmanuelle MONTARGES-PELLETIER<sup>1,2,\*</sup>, Renaud GLEY<sup>1</sup>, Valérie  
4           BRIOIS<sup>3</sup>, Laurent MICHOT<sup>4</sup>, Hussein KANBAR<sup>1,2</sup> Céline CAILLET<sup>1</sup>, Angelina  
5           RAZAFITIANAMAHARAVO<sup>1</sup>, Frédéric VILLIERAS<sup>1</sup>

6           <sup>1</sup> *Université de Lorraine, CNRS, LIEC, F- 54000 Nancy, France.*

7           <sup>2</sup> *LTSER Zone Atelier Moselle, F-54000 Nancy, France*

8           <sup>3</sup> *Synchrotron SOLEIL, L'Orme des Merisiers, Saint Aubin BP48, 91192 Gif sur Yvette cedex, France*

9           <sup>4</sup> *Sorbonne Université CNRS, Phenix Physicochimie des Electrolytes et Nanosystèmes Interfaciaux. 4,  
10           Place Jussieu 75005 Paris.*

11           \* *corresponding author emmanuelle.montarges@univ-lorraine.fr*

12           **ABSTRACT**

13           River Suspended Particulate Matter (SPM) is playing a crucial role in the fate and behavior of  
14           pollutants such as Zn, a widespread trace metal commonly encountered in continental surface  
15           waters. SPM is constituted of particles and colloids and is described as complex, heterogeneous  
16           particles composed by mineral, organic and microbiological components with high surface  
17           reactivity. In this study, the surface properties of river SPM and its capacity to bind Zn were  
18           probed using electrophoretic mobility (EM) experiments, specific surface area (SSA)  
19           measurements, Zn adsorption tests and X-ray Absorption Spectroscopy experiments (XAS).  
20           The external characteristics and reactivity of lab-controlled mineral phases (illite, Ferrihydrite,  
21           illite-iron (hydr)oxide composite, calcite) were investigated as for natural SPM. Electrophoretic  
22           mobility (EM) of the SPM exhibited low variations among the samples and was essentially  
23           assigned to the clay particles that predominate the mineralogical composition. Zn sorption  
24           experiments evidenced comparable adsorption capacity except for two samples in relation with  
25           their different mineral and chemical composition. Zn K-edge XAS data revealed that at low Zn  
26           loadings, the binding mode of this metal with environmental particles was controlled by the  
27           mineralogical composition. Indeed, Linear Combination Fitting of XAS curves, completed by  
28           shell-to-shell fitting revealed Zn association to SPM by surface complexation. XAS results  
29           showed that for SPM samples collected in high flow regime, Zn was mainly bound to clay  
30           minerals. In contrast, for the SPM sample collected during low flow regime, Zn was not only  
31           bound to clay mineral but also to iron (hydr)oxides.

32           **Key words: Suspended Particulate Matter, River, Zn, lab-controlled minerals, surface reactivity,  
33           binding mode, X-ray absorption spectroscopy.**

## 31 1. INTRODUCTION

32 The development of human activities since the end of the XIXth century resulted in a strong  
33 increase in the extraction of metallic ores, which provoked a strong increase of trace metal  
34 deposition in environmental media (Nriagu and Pacyna, 1988; Viers et al., 2009). Among those  
35 trace metals, Cu, Zn and Pb are the most commonly encountered worldwide and are frequently  
36 occurring in urban areas, and thus in domestic waste waters or run-off waters from artificial  
37 surfaces (roads, roofs, parking lots, pavements etc). Zinc is a common contaminant in  
38 continental rivers (Grosbois et al., 2012; Juillot et al., 2011; Le Pape et al., 2014, 2012; Priadi  
39 et al., 2012; Superville et al., 2011; Yin et al., 2015) and was found to be predominantly  
40 associated to the suspended matter (Le Meur et al., 2016; Resongles et al., 2015; Viers et al.,  
41 2009). In order to better predict Zn fate and behaviour in rivers, it is necessary to unravel the  
42 interaction between Zn and environmental particles, such as suspended particulate matter or  
43 SPM. River SPM encompass particles and colloids, and are commonly described as complex  
44 and heterogeneous aggregates composed by mineral, organic and microbiological components  
45 (Stumm, 1993). The affinity of natural surfaces towards trace metals was evidenced through  
46 metal adsorption experiments on environmental matrices, such as soils, sediments or river SPM  
47 (Bengtsson and Picado, 2008; Bibby and Webster-Brown, 2006; Buyang et al., 2019; Covelo  
48 et al., 2007; Wang et al., 1997; Young and Harvey, 1992). These studies unraveled the crucial  
49 role of particle size, morphology, composition and structural irregularities of the  
50 submicrometric constituents and repeatedly demonstrated the major role of Fe-(hydr)oxide and  
51 clay mineral surfaces. In order to better understand the affinity of natural particles towards  
52 metals such as Zn, and for establishing quantitative models to predict Zn behaviour in natural  
53 media, numerous lab-controlled investigations on model or synthetic adsorbents, under  
54 controlled conditions (pH, temperature, ionic strength, time), were thus performed to identify  
55 adsorption mechanisms and the nature of the binding mode(s) (Churakov and Dähn, 2012;

56 Cismasu et al., 2013; Dähn et al., 2011; Davis et al., 1998; Dyer et al., 2004; Lee et al., 2004;  
57 Miyazaki et al., 2003; Montoya et al., 2018; Nachtegaal and Sparks, 2004; Schlegel et al., 2001;  
58 Schlegel and Manceau, 2006; Sipos et al., 2018; Tertre et al., 2009; Toner et al., 2006; Trivedi  
59 et al., 2004, 2001a, 2001b). However, only a limited number of studies dealing with metal  
60 adsorption mechanisms on model mineral phases, tried to explicitly consider the complexity  
61 and heterogeneity of environmental particles.

62 Furthermore, a crucial question remains about the extrapolation of theoretical adsorption  
63 models obtained on pure and single mineral phases to environmental particles. Can we compare  
64 river SPM reactivity (towards Zn for instance) with that of pure mineral phases (e.g. illite,  
65 ferrihydrite, goethite, calcite)? Also, as soon as we assume that river SPM is formed of mineral  
66 assemblies, what will be the real availability of adsorption sites and reactive surface groups?  
67 Such an issue is important to address since those chemical groups might be partially involved  
68 in the mineral-mineral interactions or mineral-organic interactions (Chen et al., 2004;  
69 Zimmermann-Timm, 2002). This paper investigated River SPM reactivity towards Zn, and  
70 compared it to that of pure mineral phases including clay minerals (illite), iron (hydr)oxides  
71 (ferrihydrite and goethite) and calcite. Those mineral phases were selected since clay minerals  
72 were shown to be predominant in most continental river SPM (Manickam et al., 1985; Slomberg  
73 et al., 2016) and particularly for Moselle River SPM (Le Meur et al., 2016). In addition, to try  
74 to better approach natural complexity, the reactivity of a composite mineral obtained from the  
75 hydrolysis of iron in the presence of illite platelets was also investigated.

76 To provide evidence for the role of SPM components in Zn fate, Zn adsorption isotherms were  
77 interpreted regarding external characteristics such as textural properties (gas adsorption  
78 experiments), surface charge (electrophoretic mobility), or cationic exchange capacity whereas  
79 the binding modes of Zn were investigated through X-ray absorption spectroscopy experiments.



## 80 2. MATERIALS AND METHODS

### 81 2.1 Study site and SPM samples

82 River SPM samples were collected from Moselle River and tributaries, within the French  
83 Moselle catchment, in the north-eastern part of France. Sampling stations along the Moselle  
84 River and tributaries were selected to screen the Zn association mode in SPM, and will be  
85 referred to as follow in the text: FRO for Frouard, PSV for Pont-Saint-Vincent, MIL for Millery;  
86 PAM for Pont-a-Mousson, ARG for Argancy; FLO for Florange and THI for Thionville FRO,  
87 MIL, PAM, ARG and THI are Moselle River stations, following a gradient of urbanization of  
88 the watershed. PSV is a station on the Madon River, FLO is a station on the Fensch River Those  
89 three stations on tributaries are located close to the junction with Moselle river. More  
90 information is available in previous publications (Le Meur et al., 2017, 2016) as well as on the  
91 data repository ORDAR (appendix A <https://doi.org/10.24396/ORDAR-62>). Numerous SPM  
92 samples from the station Frouard or FRO on Moselle River, were collected between November  
93 2012 and March 2015 (Table 1). For SPM collection, River water was pumped and sent to a  
94 continuous flow field centrifuge (CEPA Z-41 20000 rpm, equivalent to 17000 g). The flow rate  
95 of the pumping was set to 600 L h<sup>-1</sup>. Such a collection method guaranteed the representativeness  
96 of SPM samples as up to one hundred grams were collected corresponding to 1 or 2 m<sup>3</sup> of  
97 centrifuged water. Turbidity and grain size distribution of river water entering and exiting the  
98 centrifuge bowl were checked during the whole sampling to assess the performance of the field  
99 centrifuge. The size cut-off of retained particles was approximately 3 μm and was checked with  
100 laser diffraction analysis of centrifuge input and output at different times during field  
101 centrifugation (laser diffraction instrument SYMPATEC). SPM were gently recovered from  
102 the Teflon plates covering the internal surface of the centrifuge bowl and were immediately  
103 frozen and freeze-dried for analytical purpose. The samples were dialyzed with ultrapure water  
104 during 2 or 3 days, until the electrical conductivity was below 5 μS cm<sup>-1</sup>. The elemental

105 composition of SPM samples can be found in Appendix A (<https://doi.org/10.24396/ORDAR->  
106 [62](https://doi.org/10.24396/ORDAR-62)).

107

## 108 **2. 2. Model compounds**

### 109 *2.2.1. Illite purification.*

110 The raw clay mineral sample Illite du Puy (Argile du Velay) was characterized by X-ray  
111 diffraction (XRD). XRD patterns revealed the presence of quartz, feldspar, kaolinite and calcite  
112 as the accessory minerals. Then, prior to use, the raw clay mineral sample was purified and  
113 homo-ionized with sodium (Blachier et al., 2014). A 40 g L<sup>-1</sup> illite suspension was first mixed  
114 with 1M sodium acetate solution set to pH 5 by addition of acetic acid (0.1 M) to remove  
115 carbonates. After centrifugation (7,500 rpm, 45 min), the solid was exchanged three times using  
116 1 M NaCl solution. The suspension was then dialyzed several times in deionized water until the  
117 water was chloride free (conductivity below 5  $\mu\text{S cm}^{-1}$ ). Clay suspension was then centrifuged  
118 in order to separate the different clay size fractions. Centrifuging during one hour with 25,700 g  
119 resulted in two size fractions referred to as illite-s2 (bottom particles) and illite-s3 (supernatant).  
120 A second centrifugation during 45 min with 34,800 g provided a smallest size fraction referred  
121 to as illite-s3bis. TEM observations on the illite-s3 and illite-s3bis fractions evidenced a rather  
122 homogeneous clay phase, in size and composition (Appendix B, supplementary information  
123 can be found there <https://doi.org/10.24396/ORDAR-28>). The size fraction illite-s3 was  
124 selected for the adsorption experiments and for the preparation of clay-composites with  
125 ferrihydrite.

126

### 127 *2.2.2. Ferrihydrite synthesis.*

128 Ferrihydrite (FeH) was synthesized following the method proposed for the 2-line FeH (Cornell  
129 and Schwertmann, 2003). Ferric solution was prepared using 0.1 M of the nitrate salt

130  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ . A solution of KOH 1 M was added to the ferric solution to bring the pH to 8.  
131 Then, the suspension was stirred for 1 h and centrifuged (10 min, 7,000 rpm). Ferrihydrite was  
132 frozen and freeze-dried prior to analyses and adsorption experiments.

133

### 134 2.2.3. *Illite-iron (hydr)oxide composite.*

135 A clay composite, on the basis of illite and iron (hydr)oxide, was prepared to mimic the presence  
136 of iron (hydr)oxide coatings evidenced on natural particles (Le Meur et al., 2016; Nachtegaal  
137 and Sparks, 2004). This mixed sample was referred to as Illite-FeH, and was prepared as  
138 follows: 100 mg of purified illite was suspended in 100 mL of ultra-pure water. Fe(III) nitrate  
139 solution (0.001 M, pH 4) and KOH solution (0.01 M) were simultaneously added to the illite  
140 suspension (pH 6.6) using a twin syringe pump (Harvard Apparatus). KOH solution was added  
141 at  $0.2 \pm 0.05$  ml/min and Fe(III) nitrate solution was added at  $0.5 \pm 0.05$  ml/min. The pH of this  
142 suspension was checked continuously, and the speed of addition was adjusted in order to avoid  
143 strong decrease of pH values (pH remained  $\geq 5.0$ ). The amount of Fe was equivalent to two  
144 times the cation exchange capacity (CEC) of illite (table 1), and KOH addition was stopped  
145 when pH 7 was reached. The resulting suspension was then stirred for 1 h and the final  
146 suspension was rinsed three times with ultrapure water to remove excess  $\text{K}^+$ ,  $\text{NO}_3^-$  ions. The  
147 aggregates were collected by centrifugation (15 min with 9000g), and freeze-dried. This method  
148 was selected to avoid strong pH variations that might weather illite minerals or provoke the  
149 precipitation of iron oxy-hydroxide in solution. This procedure is then slightly different from  
150 those reported by (Liljestrand et al., 1992) and (Green-Pedersen and Pind, 2000). Furthermore,  
151 the relatively low Fe concentration was selected not only to be closer to iron concentrations in  
152 surface waters, but above all to favour iron oxy-hydroxide precipitation onto clay mineral  
153 surfaces and to enhance homogeneous distribution of iron hydroxide particles on clay platelets.

### 154 2.2.4. *Supplementary model minerals*

155 Supplementary model minerals, goethite and calcite were also included in those investigations.  
156 Pure synthetic goethite (Sikovit 10E172) was purchased from BASF (Germany). The goethite  
157 particles are well-crystallized needles of an average size of 600 nm × 100 nm × 10 nm. (Prélot,  
158 2001; Prélot et al., 2002). Calcite originated from Marocco (El Hammam mine, Meknes,  
159 Marocco), its purity was checked through XRD.

160 Ultra-pure water and American Chemical Society reagent-grade chemicals or better were used  
161 for all experiments. Glassware was soaked in 1 M HNO<sub>3</sub> for at least 12 h and rinsed three times  
162 prior to use.

163

## 164 **2. 3. Methods for sample characterization**

### 165 *2.3.1. Electrophoretic mobility measurements*

166 Electrophoretic mobility (EM) was measured with a zeta-phoremeter (Zetaphoremeter IV-CAD  
167 Instrumentations) equipped with a video interface via CCD camera. Measurements were carried  
168 out in a diluted suspension of SPM at constant ionic strength (NaNO<sub>3</sub>, 0.01 mol/L), varying pH  
169 from 3 to 11 by adding acid (HCl) or base (NaOH) to the SPM suspension. The standard  
170 deviation provided with the EM values reports the distribution of particle velocities collected  
171 by the CCD camera, no bimodal distribution could be evidenced, and all the measurements on  
172 model and environmental particles provided a continuous distribution of electrophoretic  
173 mobilities.

174

### 175 *2.3.2. Cation Exchange Capacity*

176 Cation Exchange Capacity (CEC) was measured using the cobalt-hexamine trichloride  
177 (Co(NH<sub>3</sub>)<sub>6</sub>Cl<sub>3</sub>) method (Ciesielski and Sterckeman, 1997; Orsini and Remy, 1976).

178 1.5 g of sample was dispersed and shaken during two hours at 30°C in 30 mL of cobalt-  
179 hexamine solution (16.6 × 10<sup>-3</sup> mol L<sup>-1</sup>). Samples were then centrifuged for one hour at 46,250

180 g. Supernatants were subsequently analysed on a UV–Visible spectrophotometer, using the  
181 intensity of the absorption band at 472 nm to evaluate residual concentration of cobalt-  
182 hexamine and derive the CEC of the solid. CEC was also estimated from the concentrations of  
183 released cations and concentrations of Na, K, Ca, Mg, Fe, Al and Si in supernatants were  
184 measured by atomic absorption, using a Perkin Elmer AA800 set-up (CRPG, Vandœuvre-lès-  
185 Nancy) to calculate CEC from the sum of exchanged cations. Measurements were always  
186 carried out in duplicate.

187

### 188 *2.3.3. Nitrogen adsorption for textural characterization*

189 Nitrogen adsorption-desorption isotherms at 77 K were recorded on a step-by-step automatic  
190 set-up (BET 2000). Prior to adsorption experiments, SPM and pure minerals (from 0.1 to 1 g)  
191 were outgassed at 50°C during 18 hours under a residual vacuum of 0.01 Pa (30°C for FeH and  
192 illite-FeH in order to not alter the iron (hydr)oxide (Hofmann et al., 2013). Specific Surface  
193 Areas (SSA) were determined from the Brunauer-Emmet-Teller (BET) equation (Brunauer et  
194 al., 1938) using  $16.2 \text{ \AA}^2$  as the cross-sectional area for nitrogen molecules. The De Boer method  
195 (or  $t$ -plot) was carried out to determine microporous volume and external surface area.  
196 Micropore filling happens at low and very low relative pressure values, and then includes the  
197 domain of the monolayer adsorption on external surface. To be able to distinguish adsorption  
198 onto external surface from adsorption into the micropores (pore size  $< 20 \text{ \AA}$ ), the experimental  
199 isotherm is compared to a reference curve obtained for a non-porous solid, with chemical  
200 features and energetic constant as close as possible to the studied matrix.

201

### 202 *2.3.4. Zn adsorption isotherms, batch experiments*

203 Adsorption isotherms were performed on SPM samples and pure minerals. They were obtained  
204 from batch experiments by varying Zn concentration in solution and using a constant  
205 solid/liquid ratio of  $285 \text{ mg L}^{-1}$ . This ratio was selected based on experimental feasibility, and

206 to be able to run spectroscopic measurements at Zn K-edge at the end of adsorption  
207 experiments. The temperature was fixed at 25 °C, the pH of aqueous solution was fixed to pH  
208 7.0 ( $\pm 0.2$ ) and the ionic strength was fixed either at 300  $\mu\text{S}\cdot\text{cm}^{-1}$  or 3000  $\mu\text{S}\cdot\text{cm}^{-1}$  using  $\text{NaNO}_3$   
209 solution in order to study the effect of conductivity on Zn adsorption. The mass of solid ( $m$ )  
210 was fixed to 10 mg and added to a volume ( $V$ ) of 35 mL of Zn solution of fixed concentration  
211 ranging from 1 – 500  $\mu\text{mol L}^{-1}$  in a 40 ml polyethylene centrifuge bottle. The mixture was then  
212 shaken in a thermo stated (25°C) chamber overnight. The mixture was centrifuged at 19000  
213 rpm during 20 min and the supernatant was filtered using 0.22  $\mu\text{m}$  syringe filters. The solutions  
214 were acidified, and initial and equilibrium Zn concentrations were determined by atomic  
215 absorption, using a Perkin Elmer AA800 set-up (CRPG, Vandœuvre-lès-Nancy, France). The  
216 amount of Zn adsorbed on solid ( $Q_{\text{ads}}$ ) was obtained from the difference between the initial  
217 ( $C_i$ ) and the equilibrium ( $C_e$ ) concentrations using the formula:  $Q_{\text{ads}} = (C_i - C_e) * \frac{V}{m}$ . The  
218 solid fraction of each sample was collected, frozen, freeze-dried and pelletized prior to XAS  
219 analysis. Each Zn adsorption experiment was performed using ten different Zn concentrations  
220 referred to as  $\text{Zn}_i$ ,  $i = 1$  to 10. The Zn initial concentrations are for  $i = 1$  to 10, 1  $\mu\text{mol L}^{-1}$ , 2  
221  $\mu\text{mol L}^{-1}$ , 5  $\mu\text{mol L}^{-1}$ , 10  $\mu\text{mol L}^{-1}$ , 20  $\mu\text{mol L}^{-1}$ , 50  $\mu\text{mol L}^{-1}$ , 100  $\mu\text{mol L}^{-1}$ , 200  $\mu\text{mol L}^{-1}$  and  
222 500  $\mu\text{mol L}^{-1}$  respectively. The solid samples resulting from the Zn adsorption experiments are  
223 referred to as  $\text{SPM}_{\text{name}}\text{Zn}_i$ ,  $i$  stating for the position on the Zn adsorption curve.  
224 Supplementary Zn adsorption experiments were performed with higher ionic strength, *i.e.*,  
225 electric conductivity was set to 3000  $\mu\text{S}\cdot\text{cm}^{-1}$  instead of 300  $\mu\text{S}\cdot\text{cm}^{-1}$ . A suffix  $3k$  was added to  
226 the name of samples. Such batch experiments were performed for different SPM samples and  
227 also for synthetic and pure mineral phases: illite, illite-FeH, and goethite. The end-members of  
228 the adsorption isotherms, *i.e.*, lowest and highest Zn loadings, were used as references for XAS  
229 and were respectively referred as to  $\text{Zn}_{\text{low}}\text{-Illite}$ ,  $\text{Zn}_{\text{high}}\text{-Illite}$ ,  $\text{Zn}_{\text{low}}\text{-Illite-FeH}$ ,  $\text{Zn}_{\text{high}}\text{-Illite-}$   
230  $\text{FeH}$ ,  $\text{Zn}_{\text{high}}\text{-FeH}$  and  $\text{Zn}_{\text{high}}\text{-Goethite}$ . In order to prepare supplementary Zn bearing phases as

231 reference samples for XAS spectroscopy, the same protocol was used with calcite. Those latter  
232 batch experiments provided two different samples for XAS, (i) Zn adsorbed onto calcite  
233 referred as to Zn<sub>low</sub>-Calcite, obtained with initial concentration in Zn(NO<sub>3</sub>)<sub>2</sub> set at 10<sup>-6</sup> mol L<sup>-1</sup>,  
234 and displaying a Zn loading of 120 mg kg<sup>-1</sup>; (ii) Zn coprecipitated onto calcite, referred as to  
235 Zn<sub>high</sub>-Calcite, obtained with initial concentration in Zn(NO<sub>3</sub>)<sub>2</sub> set at 5.10<sup>-4</sup> mol L<sup>-1</sup>, and  
236 displaying a Zn:Ca ratio of 0.16:1.

237

### 238 *2.2.5 XAFS data collection and analysis*

239 Most of the X-ray absorption spectra were collected at SAMBA beamline of the French  
240 National synchrotron facility SOLEIL located in Gif-sur-Yvette, France and a few  
241 complementary spectra (high Zn contents) were measured at the XAFS beamline from the  
242 Italian synchrotron facility ELETTRA (Trieste, Italy). The synchrotron ring was running at 2.75  
243 GeV (SOLEIL) and at 2 GeV (ELETTRA) with an average current of 400 mA (SOLEIL) and  
244 309 mA (ELETTRA). The X ray beam was monochromatized using a set of Si (220) on  
245 SAMBA beamline and Si (111) crystals on XAFS beamline. Experimental measurements were  
246 made at the Zn K-edge (9659 eV) and XAS spectra were collected in fluorescence detection  
247 mode using a CANBERRA 36 elements Ge detector on SAMBA and in transmission mode on  
248 XAFS beamline at Elettra. For all synchrotron sessions, the samples were prepared as pellets  
249 with at least 30 % of cellulose to increase the cohesive character of the pellet. The pellets were  
250 placed at 45° angle with respect to the incident beam for fluorescence and at 90° for  
251 transmission. All the spectra were collected using a cryostat chamber filled with liquid nitrogen  
252 at a temperature close to 77 K or -192 °C. Such a low temperature was sufficient to minimize  
253 thermal dampening of the EXAFS signal, and to slow down potential beam damage due to the  
254 presence of natural organic matter in the environmental samples. Between 4 and 6 scans were  
255 collected per sample to improve the signal to noise ratio.

256 Data extraction was performed using Athena software (Newville, 2001; Ravel and Newville,  
257 2005). In order to calibrate energy for each Zn edge individual spectrum, a reference spectrum  
258 was obtained from a Zn foil set behind ionization chamber for transmitted beam. The first  
259 inflection point (zero on the second derivative) of the absorption edge was systematically set at  
260 9659 eV for Zn foil spectra. For every sample spectrum,  $E_0$  was set at the maximum of the first  
261 derivative of the absorption edge.  $k^3$ -weighted EXAFS were obtained from the background-  
262 subtracted and normalized spectra. Linear combination fitting (LCF) was performed on  
263 XANES and EXAFS regions of XAS spectra using ATHENA program (Isaure et al., 2002;  
264 Manceau et al., 1996). References were selected on the basis of SPM characterization and  
265 mineral phases identified (Le Meur et al., 2016).

266 For XANES, LCF fitting samples and reference spectra were all normalized in the same energy  
267 domain [20, 150] after  $E_0$ . Fitting was performed on a restrained energy domain, -20 +120  
268 around  $E_0$ , with a maximum number of components set to 3 and the sum of contributions forced  
269 to be equal to 1. Fitting solution was judged by the lowest  $R_x$  factor ( $R_x =$   
270  $\sum_n (\mu_{exp} - \mu_{fit})^2 / (\mu_{exp})^2$ ) and the number of components was increased only if it resulted in  
271 a consistent decrease of  $R_x$  (10%). The fitting solution was selected not only from the lowest  
272 residual component but also from visual appreciation and in particular we took into account the  
273 good reproduction of spectral features in the edge area, including the splitting of the edge when  
274 it was obvious. For EXAFS region,  $E_0$  was set at the same value for all spectra in order to  
275 calculate  $\chi(k)$  oscillations in the same  $k$  range. Fitting was performed on 3-11  $\text{\AA}^{-1}$   $k$  range with  
276 4 components as a maximum. Quality of fit was checked with the fitting factor  $R_e$  ( $R_e =$   
277  $\sum_n (k^3 \chi_{exp} - k^3 \chi_{fit})^2 / (k^3 \chi_{exp})^2$ ), but also with qualitative appreciation on Fourier  
278 transforms (magnitude and imaginary parts).

279 We considered that those LCF results provided fractions of individual Zn bearing phases with  
280 a precision of about 10%. Limits and discussion about this fitting method have been previously



281 reported (Isaure et al. 2002). Shell-by-shell fitting was performed using the Artemis routine  
282 from the IFEFFiT software (Newville, 2001; Ravel and Newville, 2005). The amplitude  
283 reduction factor ( $S_0^2$ ) was fixed at 0.7 for all shells. A good fit was determined on the basis of  
284 the minimum residual error  $R_e$ , calculated with the same formulas for LCF.

285 Beside the reference samples already mentioned, additional reference spectra were obtained  
286 from Zn-citrate and Zn-oxalate solutions (in fluorescence mode using a solution holder), from  
287 a Zn-rich trioctahedral smectite, sauconite, provided by Stephan Kaufhold (Kaufhold et al.,  
288 2015), and from other reference minerals: zincite, a double layer hydroxide Zn-HDL provided  
289 by V. Briois (Carvalho et al., 2013; Roussel et al., 2001), amorphous zinc sulphide, wurztite  
290 (ZnS), sphalerite (ZnS), a silicate, willemite ( $Zn_2SiO_4$ ), and two spinels, gahnite ( $ZnAl_2O_4$ ) and  
291 franklinite ( $ZnFe_2O_4$ ) supplied by the French National Museum of Natural History (Paris,  
292 France). The XANES and EXAFS data collected at Zn K-edge can be found in Appendix C  
293 (<https://doi.org/10.24396/ORDAR-26>).

294

### 295 **3. RESULTS**

#### 296 **3.1 Surface Properties of SPM samples and comparison to model particles.**

##### 297 *3.1.1 Electrophoretic mobility (EM) and Cationic Exchange Capacity (CEC)*

298 Figure 1 shows the electrophoretic mobility (EM) curves obtained for the different model  
299 particles suspended in aqueous solution ( $NaNO_3$  0.01 mol/L, pH adjusted from 3 to 11). The  
300 illite particles display a negative EM curve for all the different pH values.

301 Those results were similar for both size fractions of illite and are close to those previously  
302 determined on purified illite (Sondi et al., 1996). EM curve is dominated by the contribution of  
303 the structural and thus permanent charge of illite particles, beside the variable surface charge  
304 due to amphoteric edges. In comparison with other clay minerals, EM of illite particles tends  
305 to show slight variations with pH, going towards less negative values in the acidic pH range [2

306 to 6] and towards more negative values for basic values of pH. This indicates a relatively large  
307 fraction of amphoteric edges, but not to the extent of reaching positive EM in the conditions of  
308 the measurements.

309 Although illite displays a relatively high density of charge, the contribution of variable charge  
310 is enhanced by the size and shape of particles, and also the stage of aggregation, itself influenced  
311 by the density of layer charge and location in the layer (Thomas et al., 1999). EM measured for  
312 the iron oxyhydroxide, ferrihydrite, did not display the same trend as amphoteric surface sites  
313 mainly govern it. The mixed compound illite-FeH displays similar results to that of illite,  
314 suggesting that the charge of the mixed particles is close to that of the pristine illite, and that  
315 aggregation state is rather close to that of pristine illite. However, the presence of iron oxy-  
316 hydroxide coatings is unravelled by a slight modification of mobility at pH below 6. The low  
317 extent of standard deviation also suggests a relative homogeneity of the mixed minerals.

318 Electrophoretic mobility was measured for distinct SPM samples, and two curves are presented  
319 on Figure 1 (other curves are presented as supplementary material). For both samples the EM  
320 is negative on the whole pH range suggesting the strong contribution of permanent negative  
321 charge, such as illite, directly related to the mineralogical composition of SPM, mainly  
322 constituted of clay minerals (Le Meur et al., 2016). In agreement with this assumption, the  
323 sample FRO-Jul13, relatively depleted in clay minerals, displays a less negative electrophoretic  
324 mobility than the sample FRO-Dec12. However, considering the range of values, as well as the  
325 associated standard deviations, one can consider that those two SPM samples are rather close  
326 in terms of electrophoretic mobility. Moreover, the standard deviations (see material and  
327 methods part for their meaning), evidence that those samples are relatively disperse and  
328 heterogeneous, certainly constituted of particles with different electrophoretic behaviour. When  
329 comparing those SPM samples with the illite mineral (Figure 1), the presence of clay minerals  
330 or negatively charged minerals is confirmed but their nature and/or shape might vary

331 consistently, resulting in a relatively more pronounced shift towards less negative values at low  
332 pH conditions. This difference of EM between SPM and illite can be due to different factors:  
333 the presence of clay minerals with low density of charge (kaolinite, montmorillonite, chlorite)  
334 and also the aggregation stage, reinforced by the presence of hydroxide coatings and organic  
335 matter (Chorom and Rengasamy, 1995; Thomas et al., 1999; Zhuang and Yu, 2002).  
336 The cationic exchange capacities obtained for the different SPM samples are presented in Table  
337 1. They are in the same range of order, and slightly higher than the CEC measured for the  
338 reference illite; these higher values can be explained by the presence of montmorillonite layers  
339 that are commonly displaying higher CEC values than illite minerals, and/or by the cation  
340 exchange capacity of organic matter (Parfitt et al., 1995). For FRO samples, we could not really  
341 evidence a relation between the CEC value and the organic matter content of SPM.

342

### 343 *3.1.2. Textural properties*

344 The specific surface areas (SSA) were measured for the different synthesized particles and are  
345 presented in the Table 1. The SSA is the highest for the FeH ( $218 \text{ m}^2 \text{ g}^{-1}$ ). The illite displays a  
346 lower SSA ( $155 \text{ m}^2 \text{ g}^{-1}$ ) and the illite-FeH sample presents a lower SSA of  $124 \text{ m}^2 \text{ g}^{-1}$ ,  
347 suggesting a reduction of accessible surface due to the presence of Fe-precipitates. The SSA  
348 was also measured for natural river SPM samples. SSA ranged between 6 and  $37 \text{ m}^2 \text{ g}^{-1}$  and we  
349 could evidence an anti-correlation between these values and the organic matter content  
350 determined by thermogravimetric analyses (Le Meur et al., 2017). This relationship is also  
351 consistent with the increase of fine particles occurring with the increase of regime flow (in the  
352 range of these investigations, see Le Meur et al. 2016).

353 Then the influence of organic matter on textural properties of river SPM can be seen as a double  
354 effect, increasing the mean particle size through enhanced flocculation, and decreasing the  
355 specific surface area through the lower accessibility of external sites, at least for nitrogen

356 molecules. Based on nitrogen adsorption, none of the river samples displays a significant  
357 equivalent microporous surface area (always  $\leq 1 \text{ m}^2 \text{ g}^{-1}$ ) while the model particles, except  
358 goethite, show a microporous surface area ranging between 28 and  $47 \text{ m}^2 \text{ g}^{-1}$ .

359

## 360 **3.2. Zn adsorption isotherms: batch experiments as a function of Zn concentration**

### 361 *3.2.1. Zn adsorption on lab-controlled mineral phases*

362 These experiments were all performed in the same conditions of pH, ionic strength and  
363 solid:liquid ratio for model and environmental solid samples. A comparison of Zn(II) uptake  
364 on Illite, FeH, Goethite and Illite-FeH is shown on Figure 2A.

365 As expected, and as previously reported (Bradbury and Baeyens, 1999; Lee et al., 2004;  
366 Nachtegaal and Sparks, 2004; Trivedi et al., 2001b, 2001a; Waychunas et al., 2003), these  
367 experiments confirm the relatively high affinity of Zn for mineral surfaces, with a strong  
368 adsorption at Zn concentrations between 0.1 and 1 micromole  $\text{L}^{-1}$ . Maximal adsorption values  
369 are 57  $\text{mmole kg}^{-1}$  for FeH, 58  $\text{mmole kg}^{-1}$  for goethite, 89  $\text{mmole kg}^{-1}$  for illite whereas illite-  
370 FeH displays intermediate adsorption capacities (75  $\text{mmol kg}^{-1}$ ). For Zn concentrations higher  
371 than 0.1  $\text{mmol L}^{-1}$ , the curve shapes suggest (i) adsorption on less energetic sites forming loose  
372 surface complexes with long-distance forces, or (ii) slow diffusion in the mineral or (iii)  
373 precipitation. In the case of illite-FeH, textural properties were similar to those of illite, and this  
374 sample shows slightly lower maximal adsorption values than illite, certainly due to the slight  
375 decrease of highly energetic sites for the adsorption of Zn (Nachtegaal and Sparks, 2004)

376

### 377 *3.4.2 Zn adsorption on River SPM*

378 Adsorption isotherms were also performed for SPM samples (Figure 2B and 2C). None of the  
379 sorption isotherms can be interpreted with the Langmuir model (Benjamin and Leckie, 1981).

380 Such an observation was expected due to the heterogeneous character of SPM composition and  
381 the high diversity of surface groups. The SPM adsorption isotherms show a relatively strong

382 adsorption for low Zn concentrations (Figure 2B) suggesting the presence of high affinity sites.  
383 Most of the SPM samples display Zn adsorption isotherms with a similar shape, except two of  
384 them, one collected from a highly impacted tributary (FLO) and one collected at the most  
385 downstream station (THI). Those two samples are rather different in terms of element  
386 concentrations, mineralogy and organic matter content. They both display high iron and organic  
387 matter contents that might explain their relatively stronger adsorption capacity (Le Meur et al.  
388 2015). Maximal adsorbed Zn values were obtained for FLO sample (547 mmol kg<sup>-1</sup>). Since  
389 those SPM were shown to be particularly rich in organic matter and iron oxyhydroxides, but  
390 rather depleted in clay minerals, it can be assumed that the strong adsorption capacity of this  
391 SPM sample was certainly due to organic matter and/or iron oxyhydroxide binding. The  
392 samples FRO-Dec12, FRO-Jul13 and FRO-Jun13 show strong similarities in terms of  
393 adsorption capacities and thus isotherm curve shape. However, FRO-Dec12 sample displays  
394 higher adsorption capacities at the beginning of the isotherm, suggesting that those river  
395 particles display a higher number of highly energetic adsorption sites. This difference of  
396 behaviour towards Zn might be due to the amount of clay minerals, higher for FRO-Dec12.  
397 Adsorption mechanisms cannot be derived from these simple batch experiments, and  
398 supplementary investigations as a function of pH, time, solid:liquid ratio, ionic strength, nature  
399 of the ions in solution (Na<sup>+</sup> vs Ca<sup>2+</sup> for instance) would certainly provide clearer assumptions.  
400 For that purpose, XAS measurements were performed to evidence the adsorption mechanisms  
401 of Zn on those natural particles. An increase in ionic strength (graph C on Figure 2) did not  
402 modify the shape of the sorption curves but the amount of adsorbed Zn is reduced for the high  
403 Zn concentrations, certainly due to the screening of the particle charge by major ions.

404

### 405 **3.5 Zn binding mode on SPM and model mineral phases**

#### 406 *3.5.1 XANES spectra obtained for Zn adsorbed onto model phases*

407 XANES spectra obtained after Zn adsorption on synthetic and purified mineral phases are  
408 presented on Figure 3. XANES features such as the position and shape of the edge are  
409 informative about Zn coordination and binding mode with the mineral surfaces (Waychunas et  
410 al., 2003).

411 On Figure 3, the XANES spectrum of Zn<sub>high</sub>-FeH (curve h), displays two well-defined peaks at  
412 9665.5 and 9669 eV. The absorption edge position suggests that Zn is partially in tetrahedral  
413 coordination. It was previously shown that Zn is adsorbed on ferrihydrite as a tetrahedral  
414 bidentate corner-sharing complex (Waychunas et al., 2003, 2002), except for very high Zn  
415 loadings, for which most of Zn remains octahedrally coordinated as in solution.

416 Cismasu et al. (2013) recorded XANES for Zn adsorbed onto FeH and Al substituted FeH with  
417 different surface coverages. They could evidence the same features as those shown on Figure  
418 3. However, they showed a third supplementary peak at 9675 eV that decreased in intensity  
419 with increasing Zn coverage, not detected in our study. They concluded as Waychunas et al  
420 (2003) that Zn was predominantly tetrahedrally coordinated when adsorbed onto ferrihydrite  
421 and onto Al- or Si-substituted ferrihydrites.

422 XANES spectrum for illite (Figure 3, curve b) displays two well-defined peaks at 9665.5 and  
423 9669 eV respectively, but with inverted intensities in comparison with that of Zn<sub>high</sub>-FeH.  
424 Furthermore, a well-defined shoulder can be observed at 9673 eV. On the opposite, for  
425 higher Zn loadings, the XANES spectrum of Zn<sub>high</sub>-illite (Figure 3, curve e) displays only one  
426 major broad peak at 9669 eV, suggesting that Zn is mainly in octahedral coordination, and with  
427 no well-defined distribution of oxygen in the first coordination shell. Those spectra were also  
428 compared to that of pristine illite that contains zinc in its crystal lattice (Figure 3, left graph,  
429 curve b, Zn-crystal-illite, Zn content 171 mg.kg<sup>-1</sup>) and to that of sauconite (Figure 3 left graph,  
430 curve a), a zinc-rich smectite, in which Zn occupies most of the octahedral layer (trioctahedral  
431 layer). For the three spectra related to sauconite, illite and Zn<sub>low</sub>-illite (Figure 3, curves a, b and

432 c), respectively, three components at 9665.5, 9669 and 9673 eV are noticeable with distinct  
433 intensity ratios. Clearly, even if Zn is assumed to keep an octahedral coordination, XANES  
434 features are relatively complex for illite and sauconite samples, and as far as we know, no  
435 theoretical model was reported to explain the different features in the edge region. The  
436 predominance of the absorption contribution at 9669 eV for the spectrum of sauconite can be  
437 explained by the relative homogeneity of local environment around Zn in that clay mineral.  
438 Indeed, since this smectite is trioctahedral (no vacant site in the octahedral layer), most Zn  
439 atoms have an identical local environment, with a similar distribution of neighbouring atoms  
440 (distance and nature). The post-edge features (at energies higher than 9680 eV) are common  
441 for both illite and sauconite, with a well-marked peak at 9686 eV and a split first oscillation  
442 with two maxima around 9710 and 9720 eV. Those post-edge features are close to those  
443 reported for Zn adsorbed onto amorphous alumina-silicate and Al<sub>2</sub>O<sub>3</sub> (Miyazaki et al., 2003).  
444 The comparison between illite and sauconite XANES spectra suggests that short-range  
445 backscattering, due to the scattering of ejected electrons by the oxygen atoms of the first  
446 coordination shell, mainly influences the post-edge features. Beside this first observation, the  
447 edge features are not only influenced by the coordination, but they are also linked to long-  
448 distance scattering and evidence the existence of distinct octahedral sites within illite. No  
449 difference is observed between Zn adsorbed on illite and on illite/FeH (Figure 3, left graph,  
450 curves c and d and curves e and f), suggesting that the presence of iron oxyhydroxides on clay  
451 minerals does not modify Zn binding or that this modification is too weak to be detected by  
452 XAS. This observation concurs with the similarity of adsorption isotherm curves and confirms  
453 that illite surface sites control Zn adsorption for this compound. The two bottom spectra (i and  
454 j curves on left graph, Figure 3) correspond to the reference samples prepared from the aqueous  
455 adsorption of Zn onto calcite. Zn<sub>low</sub>-calcite spectrum is relatively close in terms of general shape  
456 to the XANES spectrum reported for Zn adsorbed onto calcite (Elzinga and Reeder, 2002). The

457 spectrum of Zn<sub>high</sub>-calcite displays some common features to that of hemimorphite (Elzinga and  
458 Reeder, 2002) although this Zn bearing mineral was not included in our reference library, as  
459 we did not expect well-crystallized Zn bearing phases in our set of SPM samples. Both spectra  
460 show low intensity white line as well as a contribution at 9665.5 eV. Those two details suggest  
461 that Zn atoms have partially or totally a tetrahedral coordination. This assumption will be  
462 confirmed by the shell-by-shell fitting of EXAFS region (see following paragraphs, Table 3  
463 and Figure 4).

#### 464 465 3.5.2. XANES spectra obtained for Zn adsorbed onto river SPM

466 Zn K-edge XANES spectra were recorded for Moselle River SPM, before and after Zn  
467 adsorption at different Zn concentrations (Figure 3, middle and right graphs). Two SPM  
468 samples were selected on the basis of their organic matter content and mineralogy: FRO-Jul13  
469 and FRO-Dec12. Initial SPM spectra show rather similar trends with two well-defined peaks at  
470 9665.6 ( $\pm 0.2$ ) eV and 9669 ( $\pm 0.2$ ) eV for FRO-Jul13 and for FRO-Dec12.

471 However, some differences can be noticed from the two spectra and in particular in the post-  
472 edge region. FRO-Dec12 spectrum displays a sharper feature at 9687 eV and the first oscillation  
473 is split with two maxima at 9709 and 9723 eV. The post-edge features noticed on the spectrum  
474 of FRO-Dec12 suggest a contribution of Zn inserted in phyllosilicate structure as the latter split  
475 was also observed for sauconite and illite (Figure 3, curves a and b).

476 Linear combination fitting of those two XANES spectra suggested that Zn is predominantly  
477 inserted in the structure of dioctahedral clay for SPM sample FRO-Dec12, whereas the SPM  
478 sample FRO-Jul13 displays a relatively strong contribution of Zn associated with iron-  
479 oxyhydroxides (Table 2). Upon Zn adsorption, the features on SPM samples FRO-Jul13 are  
480 progressively disappearing with the increase of Zn loading (Figure 3, middle graph curves a to  
481 f). For experiments conducted with higher conductivity (curves g to i), the spectra appear  
482 smoothed with one main feature in the edge region, centred around 9669 eV. With increase of



483 Zn surface coverage, the 9665.6 eV peak, assigned to Zn inserted in octahedral layer of  
484 phyllosilicates, decreases in both cases and the general shape of XANES gets smoother and  
485 close to the spectra obtained for high Zn surface coverage of illite and illite-FeH. With  
486 increasing Zn loading, the mineral surface groups binding Zn do not influence anymore the  
487 coordination sphere of Zn, and the distribution of water molecules around Zn is not constrained  
488 by the mineral surface anymore.

489 For Zn adsorbed onto FRO-Dec12, the XANES fitting evidenced the contribution of Zn  
490 adsorbed onto calcite while the signal of Zn adsorbed onto FRO-Jul13 is predominated by Zn  
491 adsorbed onto illite and iron hydroxide ( Table 2). The role of organic matter was not readily  
492 evidenced with these spectroscopic data.

493  
494 *3.5.3. Evidence of Zn binding mode on model minerals and SPM, interpretation of EXAFS*  
495 *oscillations*

496 Association mode of Zn on model minerals and natural SPM was also investigated through the  
497 mathematical analysis of EXAFS oscillations, using both linear combination fitting and shell-  
498 by-shell fitting. EXAFS oscillations are supposed to report the spatial distribution of atoms  
499 around Zn, and in the case of complex systems, LCF using well-known Zn bearing minerals is  
500 preferred (Catalano et al., 2012; Le Pape et al., 2014; Luo et al., 2011; Scheinost et al., 2002).

501 Figure 5 presents the main reference EXAFS curves used for such linear combinations.

502 Beside Zn oxides and sulphides, the solids resulting from Zn adsorption on reference minerals  
503 (illite, calcite, goethite and ferrihydrite) were used as standard samples for the reproduction of  
504 SPM EXAFS curves. Zincite EXAFS curve displays relatively high amplitude in oscillations,  
505 due to the high crystallinity of zincite. Indeed, zincite is the only crystalline sample among the  
506 references presented on Figure 4.

507 Due to the predominance of clay minerals in natural SPM samples, and in particular illite  
508 minerals, two natural Zn bearing phyllosilicates were used as references for Zn incorporated in

509 phyllosilicate structure. EXAFS oscillations from a zinciferous smectite (sauconite, curve b on  
510 Figure 5) display a first double-bounced oscillation with maxima at 3.6 and 3.9 Å<sup>-1</sup> and a second  
511 oscillation split into two peaks at 5.1 and 5.8 Å<sup>-1</sup>. The third curve (curve c) was obtained from  
512 size-fractionated illite du Puy, a clay mineral that naturally contains Zn (about 220 mg kg<sup>-1</sup>).  
513 EXAFS oscillations display noticeable features that can be related to those previously described  
514 for zinciferous smectite: a first oscillation double-bounced at 3.5 and 4 Å<sup>-1</sup> and a second  
515 oscillation centred at 5.9 Å<sup>-1</sup> that can be described as a triple-bounced oscillation, displaying  
516 two shoulders at 5.2 and 6.4 Å<sup>-1</sup>. Those features on illite signal are typical of Zn bearing  
517 phyllosilicates with relatively low Zn content (trace level) and were previously reported,  
518 structurally interpreted and modelled (Churakov and Dähn, 2012; Dähn et al., 2011; Jacquat et  
519 al., 2008; Juillot et al., 2006; Schlegel et al., 2001). With low Zn adsorption, Zn<sub>low</sub>-illite EXAFS  
520 signal (curves c and d respectively on Figure 4) presents similar features but there is an  
521 attenuation of the scattering contribution at 3.5 Å<sup>-1</sup> and the shoulder at 5.9 Å<sup>-1</sup> is smoothed. This  
522 evolution of EXAFS signal with Zn adsorption is identical or strongly similar to that observed  
523 for montmorillonites (STx and Milos) (Dähn et al., 2011). This evolution of EXAFS signal  
524 strongly suggests that for Zn<sub>low</sub>-illite, Zn is adsorbed onto edge sites in the continuity of the  
525 octahedral sheet. For higher Zn loading (Zn<sub>high</sub>-illite, curve e), EXAFS signal is different, with  
526 a smoothed signal suggesting the predominance of outer-sphere complexes and the adsorption  
527 of Zn on weak sites, certainly including basal sites where exchangeable cations are positioned.  
528 Figure 4 also displays the EXAFS signals obtained for Zn adsorbed onto calcite (Figure 5 curves  
529 f and g). Zn adsorption onto carbonates was studied through two end-member samples, obtained  
530 with the lowest and highest initial Zn concentrations in solution, and respectively referred to as  
531 Zn<sub>low</sub>-Calcite and Zn<sub>high</sub>-Calcite. The Zn<sub>low</sub>-Calcite EXAFS signal is marked by the splitting of  
532 the first oscillation at 4 Å<sup>-1</sup> and by the presence of a low maximum at 7 Å<sup>-1</sup>. This EXAFS curve  
533 can be compared to those of smithsonite (ZnCO<sub>3</sub>) or Zn substituted calcite (Jacquat et al., 2008),

534 although in our case the Zn:Ca atomic ratio is about ten times lower than that reported by  
535 Jacquat et al (2008) for their Zn substituted calcite. Furthermore, in our study, XAS spectra  
536 were recorded at low temperature (using a liquid N<sub>2</sub> cryostat), while those reported by Jacquat  
537 et al. were obtained at ambient temperature. This different experimental parameter is known to  
538 induce differences in the global aspect of oscillations in the high  $k$  range, so the comparison  
539 between the current EXAFS signals and those reported by Jacquat et al is rather limited. The  
540 Zn<sub>high</sub>-Calcite signal is very similar to that standing for Zn adsorbed onto calcite (Elzinga et al.,  
541 2006; Elzinga and Reeder, 2002; Jacquat et al., 2009).

542 For references with high Zn loadings (Figure 5 curves e, g and h), the oscillations are dominated  
543 by the backscattering of oxygen atoms from the first coordination sphere, as already suggested  
544 by XANES spectra. Furthermore, shell by shell fitting confirmed the predominance of oxygen  
545 atoms scattering (Appendix E). Zn<sub>high</sub>-FeH curve is essentially due to the backscattering signal  
546 of oxygen atoms from the first coordination sphere, in both tetrahedral (Zn-O 1.96 Å) and  
547 octahedral (Zn-O 2.13 Å) configurations and only a minor contribution of Fe atoms as second  
548 neighbours could be evidenced. For Zn<sub>high</sub>-calcite and Zn<sub>high</sub>-illite, the same trend was observed,  
549 suggesting that Zn was bound as an outer-sphere adsorption complex or inner-sphere adsorption  
550 complex with weak backscattering from atoms of the mineral surface.

551  
552 *3.5.3. Evidence of Zn binding mode in SPM before and after Zn batch experiments,*  
553 *interpretation of EXAFS oscillations*

554 Figures 5 and 6 present the EXAFS oscillations obtained for FRO-Jul13 and FRO-Dec12 before  
555 and after Zn adsorption, as well as the corresponding Fourier Transforms. In both cases there  
556 is a clear modification of EXAFS signals with zinc adsorption. Signal modifications due to Zn  
557 adsorption are clear for both SPM samples even if Zn speciation in SPM is initially different.  
558 The Zn signal evolves in different ways for these two SPM samples. EXAFS data on original  
559 SPM samples (Figure 5 and 6, curves a) display a relatively high noise level in the high  $k$  range,

560 certainly due to a combination of the amorphous character of SPM and the low Zn content (260-  
561 300 mg kg<sup>-1</sup>). The FRO-Dec12 sample shows higher splitting of the first oscillation than the  
562 FRO-Jul13 sample, certainly due to the predominance of Zn inserted in phyllosilicate structure  
563 for this sample. Indeed, LCF suggests the predominant contribution of Zn<sub>low</sub>-illite (73 %) for  
564 FRO-Dec12. FRO-Jul13 was evaluated by LCF as the contribution of three different Zn bearing  
565 phases, Zn<sub>low</sub>-illite (about 50%), Zn<sub>high</sub>-FeH and zincite (about 25% each) (Table 3, Figure 5).  
566 Those results are consistent with the mineralogical composition of the two SPM samples, FRO-  
567 Dec12 being mainly constituted of clay minerals (Figure 7 Table 3).

568 After Zn adsorption, the increase of Zn loading on FRO-Jul13 (Figure 5 curves b to f, from the  
569 top to the bottom) induces the diminution and disappearing of the features assigned to second  
570 neighbours backscattering, at 7 Å<sup>-1</sup> and 9 Å<sup>-1</sup>. For high Zn loading, the EXAFS signal is  
571 essentially assigned to the first shell of neighbouring atoms, i.e. oxygen atoms of the  
572 coordination sphere. However, for FRO-Dec12 sample (Figure 6), the increase of Zn loading  
573 results in the splitting of the third oscillation initially centred at 7.7 Å<sup>-1</sup> that becomes a double  
574 hill at 7.3 and 8 Å<sup>-1</sup>. On Fourier Transform curves, a contribution in the 2<sup>nd</sup> or 3<sup>rd</sup> coordination  
575 sphere concomitantly appears (Figure 6, right graph R = 3.3 Å). In that case, we concluded that  
576 for FRO-Dec12 sample, the association mode of Zn was not restrained to outer sphere complex  
577 but implies also the formation of bindings with the surface of river particles.

578 Shell by shell fitting using theoretical backscattering signal was also performed for those two  
579 initial SPM samples (Figures 7 and 8, Tables 4 and 5). The theoretical fitting shows that oxygen  
580 atoms in octahedral coordination compose the first coordination shell of Zn in sample FRO-  
581 Dec12 (Zn-O 2.09 Å). For FRO-Jul13, the theoretical fitting evidences the predominance of  
582 oxygen in the first coordination sphere of Zn but the fit also suggests the contribution of S  
583 backscattering with Zn-S distances at 2.32 Å and Zn backscattering with Zn-Zn distances at  
584 3.18 and 4.15 Å (Table 4).

585 The binding of Zn onto SPM samples is fitted by the signal of Zn adsorbed onto model minerals  
586 illite, calcite and ferrihydrite (Table 3). With the increase of Zn loading, the contribution of  
587  $Zn_{high}$ illite increases for both SPM samples, and appears predominant for the highest Zn  
588 loading, FRO-Jul13 Zn10 and FRO-Dec12 Zn10. Globally, linear combination fitting of  
589 EXAFS oscillations provides results like those obtained on XANES region.

590 Shell-by-shell fitting revealed Zn surface complexation (Figure 7 and 8 Tables 4 and 5). Beside  
591 the first coordination layer, constituted of six oxygen atoms in octahedral symmetry with a  
592 bonding distance Zn-O of 2 Å, the second shell fitting shows the presence of Zn-Zn distances  
593 at 3.2 Å.

## 594 595 **4. DISCUSSION**

### 596 **4.1. Moselle River SPM reactivity - Comparison with other studies**

597 The reactivity of natural particles including their complex capacity was investigated in several  
598 studies (Borgnino et al., 2010; Ferreira et al., 1997; Lead et al., 1999; Minaberry and Gordillo,  
599 2010, 2007) targeting riverine, estuarine suspended particles or soil and sediments constituents.

600 In numerous studies, clay minerals were shown to play a major role in the complexation of  
601 metals. As mentioned by Minaberry and Gordillo, the nature and proportions of clay minerals  
602 certainly vary from one river to another, and it is crucial to consider the mineralogy of the  
603 adsorptive constituents before comparing the SPM from one river to another. In the case of the  
604 Moselle River, we could show that the contribution of clay minerals to SPM can also vary with  
605 hydrological conditions in the case of urbanized watershed (Le Meur et al., 2016) and finally  
606 we evidenced that the Zn adsorption isotherms differ slightly from one SPM sample to another.  
607 Indeed, different SPM samples were tested, displaying different clay mineral contents, different  
608 organic matter contents and different iron oxyhydroxide contents. However, excepted FLO-  
609 Oct12, the shape of Zn adsorption isotherms is rather similar, suggesting that the binding sites  
610 involved in the complexation of Zn are globally the same. Bibby and Webster-Brown (2006)

611 also performed Zn batch isotherms on river SPM. They observed almost no difference in terms  
612 of Zn adsorption between the different SPM investigated (urban versus non-urban SPM and  
613 regime flow, seasonal variations) despite some differences in composition. The Zn  
614 concentration used for their study was set to  $500 \mu\text{g L}^{-1}$  (about  $7.7 \mu\text{mol L}^{-1}$ ), close to the third  
615 point of our adsorption experiments (Zn3,  $5 \mu\text{mol L}^{-1}$ ). Zn adsorption was modelled assuming  
616 that hydrous ferric oxide (HFO) was the main adsorbing mineral surface, but the authors  
617 evidenced some discrepancies between the adsorption model and their experiments, underlining  
618 the complexity of SPM composition and the diversity of functional groups that might bind Zn.  
619 The SPM sample FLO-Oct12 states as the Fe and organic matter richest sample, and we could  
620 evidence that its capacity to sorb Zn is far much higher than that of other samples (Figure 2).  
621 In line with the previous sentences, Sipos et al. evidenced the influence of Fe content on the  
622 adsorption of four metals including Zn. Indeed, the higher the Fe content, the higher the  
623 adsorption capacity of natural particles. They also showed that the presence of Fe particles or  
624 Fe coatings on clay mineral surfaces affect the metal adsorption capacity (Sipos et al., 2018,  
625 2008). However, the Zn concentration selected for their adsorption experiments was set to 10  
626  $\text{mmol L}^{-1}$ , i.e., from twenty times to one hundred times higher than the Zn concentrations  
627 selected for our study. In order to test the influence of the presence of iron on Zn adsorption,  
628 Fe-coated illite was prepared, through a specific procedure, hydrolysing iron solution in the  
629 presence of illite particles. Although the presence of iron particles on illite surfaces was  
630 confirmed with TEM (data not shown in this publication, see Le Meur PhD manuscript (Le  
631 Meur, 2016)), the presence of these iron oxyhydroxide particles did not affect the binding mode  
632 of Zn, of if it was, we could not detect it.

633

#### 634 **4.2. Zn speciation in SPM - Comparison with other studies**

635 EXAFS results show a rather complex Zn speciation in SPM from the Moselle River, and this  
636 speciation varies with the regime flow. Few studies report Zn speciation on SPM from rivers.

637 Le Pape et al. (2014) studied Zn speciation in SPM from the Orge River, a tributary of the Seine  
638 River, located in a densely urbanized catchment. Bonnot et al. (2016) also studied three sub-  
639 catchments of the Seine watershed. In both publications, Zn was reported to be associated with  
640 ferrihydrite, calcite and clay, reported as geogenic minerals, and amorphous sulphides, assumed  
641 to appear through the mobilization of anoxic sediments of the riverbed or urban sewer system.  
642 They also reported a clear difference in speciation between low flow and high flow regime. In  
643 the Orge River, during high flow regime, for urbanized and non-urbanized stations, Zn was  
644 shown to be mainly adsorbed onto geogenic particles (calcite, clay) suggesting soil runoff and  
645 suggesting lithogenic source of Zn. During low flow regime, Le Pape et al 2014 showed that  
646 Zn was associated with amorphous SiO<sub>2</sub> and phytate, suggesting the presence of Zn adsorbed  
647 to diatoms as diatoms can sorb trace metals in such pH conditions. The sample FRO-Jul13 was  
648 also characterized by the presence of diatoms in higher content than FRO-Dec12. However, no  
649 Zn-diatom association could be deduced from the EXAFS data.

650 Voegelin et al. (2002) worked on Zn adsorption using soil columns and evidenced the formation  
651 of Zn-Al double layer hydroxide (Zn-Al LDH). This Zn species was evidenced from XAS data  
652 and more precisely from the presence of a multiple scattering feature at 8 Å<sup>-1</sup> on EXAFS curves  
653 and multiple scattering peaks at 6 Å on Fourier Transforms. Such features were absent from  
654 our EXAFS and Fourier Transform curves and the hypothetical formation of Zn-Al LDH was  
655 discarded (Voegelin et al., 2002).

#### 656 657 **4.3. Deciphering Zn binding mode in complex samples**

658 SPM samples are complex systems, constituted of environmental particles of different kinds,  
659 displaying multiple mineral phases, biological and organic matter. In this work we have tried  
660 to approach the binding mode of Zn with environmental particles combining direct and indirect  
661 methods. First, the comparison of SPM properties and Zn adsorption isotherms suggested some  
662 correlations between the composition of SPM and their reactivity. Indeed, the presence of

663 organic matter (FLO-Oct12) was evidenced for one organic-rich sample and we could assume  
664 that Zn was mainly bound to organic matter in that particular case. The two SPM samples FRO-  
665 Jul13 and FRO-Dec12 were distinct in terms of organic matter content and mineralogy. The  
666 latter was richer in inorganic components, was sampled during a flood event (see table 1) and  
667 can be considered as a real detrital sample. Beside the composition, the characterization of these  
668 two samples did not evidence clear distinction in terms of external properties. EM  
669 measurements and Zn batch adsorption experiments evidenced similar surface properties. XAS  
670 finally pointed out clear differences in the association mode of Zn. Such findings finally  
671 highlight the fact that the external properties are globally driven by the major components of  
672 the SPM samples (organic matter, clay mineralogy, iron content) but Zn adsorption reflected  
673 the presence of specific adsorption sites that are not readily related to a precise organic or  
674 mineral phase. XAS investigation of Zn adsorbed onto FRO-Dec12 evidenced the formation of  
675 inner sphere complexes.

676

677 The complexity of natural material makes the XAS data difficult to fit. Thus, the interpretation  
678 of XAS data for Zn adsorbed onto SPM is not unique. Linear combination fitting is one way to  
679 simplify the interpretation, provided that the reference library of XAS standard spectra is  
680 sufficiently exhaustive or relevant so that the spectra can be fitted with consistency and  
681 robustness.

682 However, the gap between reference standards used for LCF and environmental particles is still  
683 large and the strategy of combining several signals from pure references to mimic that of a  
684 complex mixture presents some limitations. Indeed, such a fitting procedure cannot reproduce  
685 the diversity of the chemical status of Zn in such samples. LCF procedure is commonly  
686 constrained by a preliminary PCA in order to estimate the number of components to use to fit  
687 XAFS data. Furthermore, the references to be used for fitting are selected through a target



688 transformation (Beauchemin et al., 2002). Searching for the main binding mode of Zn adsorbed  
689 onto SPM can be considered as a way to probe the reactivity of SPM and evidence the main  
690 association types that may form between the metal and the environmental particles.

691 In this work we have tried to compare model and environmental samples not only in terms of  
692 Zn binding mode but also in terms of external properties such as electrophoretic mobility,  
693 surface area, CEC. The complexity of environmental samples is difficult to reproduce or mimic  
694 and selecting rather classical mineral phases can be seen as a first step.

## 695 696 **CONCLUSION**

697 The previous paragraphs presented the detailed characterization of natural river samples  
698 including their external properties and their reactivity towards Zn, a commonly encountered  
699 metallic pollutant in continental rivers. Several bulk techniques were used including  
700 electrophoretic mobility, nitrogen adsorption experiments, batch zinc adsorption experiments  
701 and X-ray absorption spectroscopy to unravel the zinc association mode and reactivity of  
702 environmental particles. The bulk external properties of river samples could be related to their  
703 contents in organic matter and clay mineral. Indeed, the presence of clay minerals enhanced the  
704 adsorption capacity when Zn concentrations are below 1 micromole L<sup>-1</sup> while the organic matter  
705 tended to enhance the adsorption of this element for concentrations higher than 10 micromole  
706 L<sup>-1</sup>. However, surface properties (EM) and Zn adsorption were not completely predicted by  
707 organic and clay mineral contents. Furthermore, spectroscopic investigations evidenced slightly  
708 different binding modes for similar batch Zn adsorption results, revealing the complexity of  
709 environmental particles and the difficulty to predict their reactivity on the basis of bulk  
710 characterization. This study also investigated the reactivity and association mode of Zn in lab-  
711 controlled particles (illite, FeH, illite/FeH, calcite) and the pre-cited minerals were compared  
712 with river particles. Zn adsorption capacity was definitely stronger for river particles at low and  
713 high ranges of Zn concentrations, whatever the localization or hydrological conditions of

714 sampling. This second point evidenced also the difficulty to mimic environmental particles and  
715 reproduce their reactivity properties with pure mineral. These results revealed the usefulness  
716 of XANES and EXAFS investigation to probe Zn speciation in complex natural particles such  
717 as river SPM and to predict the binding mode of Zn, and finally its behavior and fate in  
718 continental waters.

719  
720 **AUTHOR CONTRIBUTION**

721 Mathieu LE MEUR wrote the first draft of the paper and Emmanuelle MONTARGES-PELLETIER  
722 wrote the final version of the paper. All the authors reviewed the final version of the paper and  
723 contributed to data collection and results interpretation. In more details, Laurent MICHOT, Valerie  
724 BRIOIS and Hussein KANBAR specifically contributed to the acquisition of XAS data. Renaud GLEY  
725 participated to the river material sampling, to the characterization of natural and reference materials and  
726 performed the cationic exchange capacity measurements. Angelina RAZAFITIANAMAHARAVO  
727 performed the textural analysis and helped for their interpretation. Celine CAILLET contributed to the  
728 measurements of electrophoretic mobility and helped for the interpretation. Emmanuelle  
729 MONTARGES PELLETIER and Frederic VILLIERAS supervised this work and Emmanuelle  
730 MONTARGES PELLETIER oversaw funding acquisition.

731  
732 **ACKNOWLEDGMENTS**

733 Region Lorraine (CPER ZAM), the French Ministry of Higher Education, Research and  
734 Innovation (PhD fellowship), and CNRS INEE (French eLTER), and the French National  
735 Agency for Research (ANR - project number ANR-14-CE01-0019) brought financial support  
736 to this work. We acknowledge SOLEIL for provision of synchrotron radiation and we would  
737 like to thank Emiliano FONDA and Andrea ZITOLO for assistance in using beamline SAMBA.  
738 We also acknowledge ELETTRA Synchrotron facility and thank Giuliana AQUILANTI and  
739 Luca OLIVI from XAFS beamline. The research leading to these results has been supported by  
740 the project CALIPSOplus under the Grant Agreement 730872 from the EU Framework

741 Programme for Research and Innovation HORIZON 2020. We also thank Sylvie MIGOT and  
742 Jaafar GHANBAJA for the access to the Transmission Electron Microscope CM200 (Institut  
743 Jean Lamour, University of Lorraine).

744

#### 745 **APPENDICES and DATA**

746 Supplementary data can be downloaded from the French Data Repository Ordar.

747 A-Elemental composition of Moselle SPM samples <https://doi.org/10.24396/ORDAR-62>

748 B-Illite data, <https://doi.org/10.24396/ORDAR-28>

749 C-Zn XAS reference spectra, <https://doi.org/10.24396/ORDAR-26>

750 [D-Electrophoretic mobility of river suspended materials.](#)

751 E-Zn references, shell by shell fitting of EXAFS oscillations for Zn<sub>low</sub>-calcite, Zn<sub>high</sub>-calcite,  
752 Zn<sub>high</sub>-ferrihydrite, Zn<sub>low</sub>-illite, Zn<sub>high</sub>-illite.

753

754 **REFERENCES**

- 755 Beauchemin, S., Hesterberg, D., Beauchemin, M., 2002. Principal Component Analysis  
756 Approach for Modeling Sulfur K-XANES Spectra of Humic Acids. *Soil Sci. Soc. Am. J.*  
757 66, 83–91. doi:10.2136/sssaj2002.8300
- 758 Bengtsson, G., Picado, F., 2008. Mercury sorption to sediments: Dependence on grain size,  
759 dissolved organic carbon, and suspended bacteria. *Chemosphere* 73, 526–531.  
760 doi:10.1016/j.chemosphere.2008.06.017
- 761 Benjamin, M.M., Leckie, J.O., 1981. Competitive adsorption of Cd, Cu, Zn, and Pb on  
762 amorphous iron oxyhydroxide. *J. Colloid Interface Sci.* 83, 410–419. doi:10.1016/0021-  
763 9797(81)90337-4
- 764 Bibby, R.L., Webster-Brown, J.G., 2006. Trace metal adsorption onto urban stream suspended  
765 particulate matter (Auckland region, New Zealand). *Appl. Geochemistry* 21, 1135–1151.  
766 doi:10.1016/j.apgeochem.2006.03.014
- 767 Blachier, C., Jacquet, A., Mosquet, M., Michot, L., Baravian, C., 2014. Impact of clay mineral  
768 particle morphology on the rheological properties of dispersions: A combined X-ray  
769 scattering, transmission electronic microscopy and flow rheology study. *Appl. Clay Sci.*  
770 87, 87–96. doi:10.1016/j.clay.2013.11.004
- 771 Borgnino, L., Garcia, M.G., del Hidalgo, M. V., Avena, M., De Pauli, C.P., Blesa, M.A.,  
772 Depetris, P.J., 2010. Modeling the Acid–Base Surface Properties of Aquatic Sediments.  
773 *Aquat. Geochemistry* 16, 279–291. doi:10.1007/s10498-009-9079-y
- 774 Bradbury, M.H., Baeyens, B., 1999. Modelling the sorption of Zn and Ni on Ca-  
775 montmorillonite. *Geochim. Cosmochim. Acta* 63, 325–336. doi:10.1016/S0016-  
776 7037(98)00281-6
- 777 Brunauer, S., Emmett, P.H., Teller, E., 1938. Adsorption of Gases in Multimolecular Layers. *J.*  
778 *Am. Chem. Soc.* 60, 309–319. doi:10.1021/ja01269a023

779 Buyang, S., Yi, Q., Cui, H., Wan, K., Zhang, S., 2019. Distribution and adsorption of metals  
780 on different particle size fractions of sediments in a hydrodynamically disturbed canal.  
781 *Sci. Total Environ.* 670, 654–661. doi:10.1016/j.scitotenv.2019.03.276

782 Carvalho, H.W.P., Pulcinelli, S.H., Santilli, C. V., Leroux, F., Meneau, F., Briois, V., 2013.  
783 XAS/WAXS Time-Resolved Phase Speciation of Chlorine LDH Thermal Transformation:  
784 Emerging Roles of Isovalent Metal Substitution. *Chem. Mater.* 25, 2855–2867.  
785 doi:10.1021/cm401352t

786 Catalano, J.G., Huhmann, B.L., Luo, Y., Mitnick, E.H., Slavney, A., Giammar, D.E., 2012.  
787 Metal release and speciation changes during wet aging of coal fly ashes. *Environ. Sci.*  
788 *Technol.* 46, 11804–11812. doi:10.1021/es302807b

789 Chen, J., Huang, D.J., Tanaka, A., Chang, C.F., Chung, S.C., Wu, W.B., Chen, C.T., 2004.  
790 Magnetic circular dichroism in Fe 2p resonant photoemission of magnetite. *Phys. Rev. B*  
791 69, 85107. doi:10.1103/PhysRevB.69.085107

792 Chorom, M., Rengasamy, P., 1995. Dispersion and zeta potential of pure clays as related to net  
793 particle charge under varying pH, electrolyte concentration and cation type. *Eur. J. Soil*  
794 *Sci.* 46, 657–665. doi:DOI: 10.1111/j.1365-2389.1995.tb01362.x

795 Churakov, S. V., Dähn, R., 2012. Zinc adsorption on clays inferred from atomistic simulations  
796 and EXAFS spectroscopy. *Environ. Sci. Technol.* 46, 5713–5719. doi:10.1021/es204423k

797 Ciesielski, H., Sterckeman, T., 1997. Determination of cation exchange capacity and  
798 exchangeable cations in soils by means of cobalt hexamine trichloride . *agronomie* 17, 1–  
799 7.

800 Cismasu, A.C., Levard, C., Michel, F.M., Brown, G.E., 2013. Properties of impurity-bearing  
801 ferrihydrite II: Insights into the surface structure and composition of pure, Al- and Si-  
802 bearing ferrihydrite from Zn(II) sorption experiments and Zn K-edge X-ray absorption  
803 spectroscopy. *Geochim. Cosmochim. Acta* 119, 46–60. doi:10.1016/j.gca.2013.05.040

804 Cornell, R.M., Schwertmann, U., 2003. The Iron Oxides: Structure, Properties, Reactions and  
805 Uses, Weinheim: Wiley-VCH. doi:10.1016/j.tca.2005.08.011

806 Covelo, E.F., Vega, F.A., Andrade, M.L., 2007. Heavy metal sorption and desorption capacity  
807 of soils containing endogenous contaminants. *J. Hazard. Mater.* 143, 419–430.  
808 doi:10.1016/j.jhazmat.2006.09.047

809 Dähn, R., Baeyens, B., Bradbury, M.H., 2011. Investigation of the different binding edge sites  
810 for Zn on montmorillonite using P-EXAFS - The strong/weak site concept in the 2SPNE  
811 SC/CE sorption model. *Geochim. Cosmochim. Acta* 75, 5154–5168.  
812 doi:10.1016/j.gca.2011.06.025

813 Davis, J.A., Coston, J.A., Kent, D.B., Fuller, C.C., 1998. Application of the surface  
814 complexation concept to complex mineral assemblages. *Environ. Sci. Technol.* 32, 2820–  
815 2828. doi:10.1021/es980312q

816 Dyer, J.A., Trivedi, P., Scrivner, N.C., Sparks, D.L., 2004. Surface complexation modeling of  
817 zinc sorption onto ferrihydrite. *J. Colloid Interface Sci.* 270, 56–65. doi:10.1016/S0021-  
818 9797(03)00618-0

819 Elzinga, E.J., Reeder, R.J., 2002. X-ray absorption spectroscopy study of Cu<sup>2+</sup> and  
820 Zn<sup>2+</sup> adsorption complexes at the calcite surface: Implications for site-specific metal  
821 incorporation preferences during calcite crystal growth. *Geochim. Cosmochim. Acta* 66,  
822 3943–3954. doi:10.1016/S0016-7037(02)00971-7

823 Elzinga, E.J., Rouff, A.A., Reeder, R.J., 2006. The long-term fate of Cu<sup>2+</sup>, Zn<sup>2+</sup>, and Pb<sup>2+</sup>  
824 adsorption complexes at the calcite surface: An X-ray absorption spectroscopy study.  
825 *Geochim. Cosmochim. Acta* 70, 2715–2725. doi:10.1016/j.gca.2006.02.026

826 Ferreira, J.R., Lawlor, A.J., Bates, J.M., Clarke, K.J., Tipping, E., 1997. Chemistry of riverine  
827 and estuarine suspended particles from the Ouse-Trent system, UK. *Colloids Surfaces A*  
828 *Physicochem. Eng. Asp.* 120, 183–198. doi:10.1016/S0927-7757(96)03721-1

829 Ford, R.G., Sparks, D.L., 2000. The nature of Zn precipitates formed in the presence of  
830 pyrophyllite. *Environ. Sci. Technol.* 34, 2479–2483. doi:10.1021/es991330q

831 Green-Pedersen, H., Pind, N., 2000. Preparation, characterization, and sorption properties for  
832 Ni(II) of iron oxyhydroxide-montmorillonite. *Colloids Surfaces A Physicochem. Eng.*  
833 *Asp.* 168, 133–145. doi:10.1016/S0927-7757(00)00448-9

834 Grosbois, C., Meybeck, M., Lestel, L., Lefèvre, I., Moatar, F., 2012. Severe and contrasted  
835 polymetallic contamination patterns (1900-2009) in the Loire River sediments (France).  
836 *Sci. Total Environ.* 435–436, 290–305. doi:10.1016/j.scitotenv.2012.06.056

837 Hofmann, A., Vantelon, D., Montargès-Pelletier, E., Villain, F., Gardoll, O.,  
838 Razafitianamaharavo, A., Ghanbaja, J., 2013. Interaction of Fe(III) and Al(III) during  
839 hydroxylation by forced hydrolysis: The nature of Al-Fe oxyhydroxy co-precipitates. *J.*  
840 *Colloid Interface Sci.* 407, 76–88. doi:10.1016/j.jcis.2013.06.020

841 Isaure, M.P., Laboudigue, A., Manceau, A., Sarret, G., Tiffreau, C., Trocellier, P., Lamble, G.,  
842 Hazemann, J.L., Chateigner, D., 2002. Quantitative Zn speciation in a contaminated  
843 dredged sediment by  $\mu$ -PIXE,  $\mu$ -SXRF, EXAFS spectroscopy and principal component  
844 analysis. *Geochim. Cosmochim. Acta* 66, 1549–1567. doi:10.1016/S0016-  
845 7037(01)00875-4

846 Jacquat, O., Voegelin, A., Kretzschmar, R., 2009. Local coordination of Zn in hydroxy-  
847 interlayered minerals and implications for Zn retention in soils. *Geochim. Cosmochim.*  
848 *Acta* 73, 348–363. doi:10.1016/j.gca.2008.10.026

849 Jacquat, O., Voegelin, A., Villard, A., Marcus, M.A., Kretzschmar, R., 2008. Formation of Zn-  
850 rich phyllosilicate, Zn-layered double hydroxide and hydrozincite in contaminated  
851 calcareous soils. *Geochim. Cosmochim. Acta* 72, 5037–5054.  
852 doi:10.1016/j.gca.2008.07.024

853 Juillot, F., Marechal, C., Morin, G., Jouvin, D., Cacaly, S., Telouk, P., Benedetti, M.F.,

854 Ildefonse, P., Sutton, S., Guyot, F., Brown, G.E., 2011. Contrasting isotopic signatures  
855 between anthropogenic and geogenic Zn and evidence for post-depositional fractionation  
856 processes in smelter-impacted soils from Northern France. *Geochim. Cosmochim. Acta*  
857 75, 2295–2308. doi:10.1016/j.gca.2011.02.004

858 Juillot, F., Morin, G., Ildefonse, P., Calas, G., Brown, G.E., 2006. EXAFS signature of  
859 structural Zn at trace levels in natural and synthetic trioctahedral 2:1 phyllosilicates. *Am.*  
860 *Mineral.* 91, 1432–1441. doi:10.2138/am.2006.1923

861 Kaufhold, S., Färber, G., Dohrmann, R., Ufer, K., Grathoff, G., 2015. Zn-rich smectite from  
862 the Silver Coin Mine, Nevada, USA. *Clay Miner.* 50, 417–430.  
863 doi:10.1180/claymin.2015.050.4.01

864 Le Meur, M., 2016. *Matières en suspension de la Moselle ( Lorraine , France ) : caractérisation*  
865 *minérale et organique et réactivité vis-à-vis des contaminants métalliques.* Université de  
866 Lorraine.

867 Le Meur, M., Mansuy-Huault, L., Lorgeoux, C., Bauer, A., Gley, R., Vantelon, D., Montargès-  
868 Pelletier, E., 2017. Spatial and temporal variations of Particulate Organic Matter from  
869 Moselle River and tributaries: A multimolecular investigation. *Org. Geochem.* 110, 45–  
870 56. doi:10.1016/j.orggeochem.2017.04.003

871 Le Meur, M., Montargès-Pelletier, E., Bauer, A., Gley, R., Migot, S., Barres, O., Delus, C.,  
872 Villieras, F., 2016. Characterization of suspended particulate matter in the Moselle River  
873 (Lorraine, France): evolution along the course of the river and in different hydrologic  
874 regimes. *J. Soils Sediments* 16, 1625–1642. doi:10.1007/s11368-015-1335-8

875 Le Pape, P., Ayrault, S., Quantin, C., 2012. Trace element behavior and partition versus  
876 urbanization gradient in an urban river (Orge River, France). *J. Hydrol.* 472–473, 99–110.  
877 doi:10.1016/j.jhydrol.2012.09.042

878 Le Pape, P., Quantin, C., Morin, G., Jouvin, D., Kieffer, I., Proux, O., Ghanbaja, J., Ayrault, S.,



879 2014. Zinc speciation in the suspended particulate matter of an urban river (Orge, France):  
880 Influence of seasonality and urbanization gradient. *Environ. Sci. Technol.* 48, 11901–  
881 11909. doi:10.1021/es500680x

882 Lead, J.R., Hamilton-Taylor, J., Davison, W., Harper, M., 1999. Trace metal sorption by natural  
883 particles and coarse colloids. *Geochim. Cosmochim. Acta* 63, 1661–1670.  
884 doi:10.1016/S0016-7037(99)00006-X

885 Lee, S., Anderson, P.R., Bunker, G.B., Karanfil, C., 2004. EXAFS study of Zn sorption  
886 mechanisms on montmorillonite. *Environ. Sci. Technol.* 38, 5426–5432.  
887 doi:10.1021/es0350076

888 Liljestrand, H.M., Lo, I.M.C., Shimizu, Y., 1992. Sorption of humic materials onto inorganic  
889 surfaces for the mitigation of facilitated pollutant transport processes, in: *Water Science*  
890 *and Technology*. doi:10.1016/j.nuclcard.2007.04.014

891 Luo, Y., Giammar, D.E., Huhmann, B.L., Catalano, J.G., 2011. Speciation of selenium, arsenic,  
892 and zinc in Class C fly ash. *Energy and Fuels* 25, 2980–2987. doi:10.1021/ef2005496

893 Manceau, A., Boisset, M.C., Sarret, G., Hazemann, J.L., Mench, M., Cambier, P., Prost, R.,  
894 1996. Direct determination of lead speciation in contaminated soils by EXAFS  
895 spectroscopy. *Environ. Sci. Technol.* 30, 1540–1552. doi:10.1021/es9505154

896 Manickam, S., Barbaroux, L., Ottman, F., 1985. Composition and mineralogy of suspended  
897 sediment in the fluvio-estuarine zone of the Loire River, France. *Sedimentology* 32, 721–  
898 741. doi:10.1111/j.1365-3091.1985.tb00484.x

899 Minaberry, Y.S., Gordillo, G.J., 2010. The influence of organic ligands on the adsorption of  
900 cadmium by suspended matter in natural waters studied by matrix-assisted laser  
901 desorption/ionization time-of-flight mass spectrometry and electrochemical methods.  
902 *Chemosphere* 78, 1356–1361. doi:10.1016/j.chemosphere.2010.01.004

903 Minaberry, Y.S., Gordillo, G.J., 2007. Complexing capacity of natural waters carrying a great

904 amount of suspended matter. *Chemosphere* 69, 1465–1473.  
905 doi:10.1016/j.chemosphere.2007.04.058

906 Miyazaki, A., Balint, I., Nakano, Y., 2003. Solid-liquid interfacial reaction of Zn<sup>2+</sup> ions on the  
907 surface of amorphous aluminosilicates with various Al/Si ratios. *Geochim. Cosmochim.*  
908 *Acta* 67, 3833–3844. doi:10.1016/S0016-7037(03)00373-9

909 Montoya, V., Baeyens, B., Glaus, M.A., Kupcik, T., Marques Fernandes, M., Van Laer, L.,  
910 Bruggeman, C., Maes, N., Schäfer, T., 2018. Sorption of Sr, Co and Zn on illite: Batch  
911 experiments and modelling including Co in-diffusion measurements on compacted  
912 samples. *Geochim. Cosmochim. Acta* 223, 1–20. doi:10.1016/j.gca.2017.11.027

913 Nachtegaal, M., Sparks, D.L., 2004. Effect of iron oxide coatings on zinc sorption mechanisms  
914 at the clay-mineral/water interface. *J. Colloid Interface Sci.* 276, 13–23.  
915 doi:10.1016/j.jcis.2004.03.031

916 Newville, M., 2001. IFEFFIT: Interactive XAFS analysis and FEFF fitting. *J. Synchrotron*  
917 *Radiat.* 8, 322–324. doi:10.1107/S0909049500016964

918 Nriagu, J.O., Pacyna, J.M., 1988. Quantitative assessment of worldwide contamination of air,  
919 water and soils by trace metals. *Nature* 333, 134–139. doi:10.1038/333134a0

920 Orsini, L., Remy, J.C., 1976. Utilisation du chlorure de cobaltihexammine pour la  
921 détermination simultanée de la capacité d'échange et des bases échangeables des sols.  
922 *Bull. l'AFES Sci. du Sol* 4, 269–275.

923 Parfitt, R.L., Giltrap, D.J., Whitton, J.S., 1995. Contribution of organic matter and clay minerals  
924 to the cation exchange capacity of soils. *Commun. Soil Sci. Plant Anal.* 26, 1343–1355.  
925 doi:10.1080/00103629509369376

926 Prélot, B., 2001. Mesure et modélisation de l'hétérogénéité énergétique à l'interface  
927 oxyde/électrolyte/métaux.

928 Prélot, B., Charmas, R., Zarzycki, P., Thomas, F., Villiéras, F., Piasecki, W., Rudziński, W.,

929 2002. Application of the theoretical 1-pK approach to analyzing proton adsorption  
930 isotherm derivatives on heterogeneous oxide surfaces. *J. Phys. Chem. B* 106, 13280–  
931 13286. doi:10.1021/jp0200573

932 Priadi, C., Le Pape, P., Morin, G., Ayrault, S., Maillot, F., Juillot, F., Hochreutener, R., Llorens,  
933 I., Testemale, D., Proux, O., Brown, G.E., 2012. X-ray absorption fine structure evidence  
934 for amorphous zinc sulfide as a major zinc species in suspended matter from the Seine  
935 river downstream of Paris, Ile-De-France, France. *Environ. Sci. Technol.* 46, 3712–3720.  
936 doi:10.1021/es2041652

937 Ravel, B., Newville, M., 2005. ATHENA, ARTEMIS, HEPHAESTUS: Data analysis for X-  
938 ray absorption spectroscopy using IFEFFIT, in: *Journal of Synchrotron Radiation*. pp.  
939 537–541. doi:10.1107/S0909049505012719

940 Resongles, E., Casiot, C., Freydier, R., Le Gall, M., Elbaz-Poulichet, F., 2015. Variation of  
941 dissolved and particulate metal(loid) (As, Cd, Pb, Sb, Tl, Zn) concentrations under varying  
942 discharge during a Mediterranean flood in a former mining watershed, the Gardon River  
943 (France). *J. Geochemical Explor.* 158, 132–142. doi:10.1016/j.gexplo.2015.07.010

944 Roussel, H., Briois, V., Elkaim, E., de Roy, A., Besse, J.-P., Jolivet, J.-P., 2001. Study of the  
945 Formation of the Layered Double Hydroxide [Zn–Cr–Cl]. *Chem. Mater.* 13, 329–337.  
946 doi:10.1021/cm001066w

947 Scheinost, A.C., Kretzschmar, R., Pfister, S., Roberts, D.R., 2002. Combining selective  
948 sequential extractions, X-ray absorption spectroscopy, and principal component analysis  
949 for quantitative zinc speciation in soil. *Environ. Sci. Technol.* 36, 5021–5028.  
950 doi:10.1021/es025669f

951 Schlegel, M.L., Manceau, A., 2006. Evidence for the nucleation and epitaxial growth of Zn  
952 phyllosilicate on montmorillonite. *Geochim. Cosmochim. Acta* 70, 901–917.  
953 doi:10.1016/j.gca.2005.10.021

954 Schlegel, M.L., Manceau, A., Charlet, L., Chateigner, D., Hazemann, J.L., 2001. Sorption of  
955 metal ions on clay minerals. III. Nucleation and epitaxial growth of Zn phyllosilicate on  
956 the edges of hectorite. *Geochim. Cosmochim. Acta* 65, 4155–4170. doi:10.1016/S0016-  
957 7037(01)00700-1

958 Sipos, P., Kis, V.K., Balázs, R., Tóth, A., Kovács, I., Németh, T., 2018. Contribution of  
959 individual pure or mixed-phase mineral particles to metal sorption in soils. *Geoderma* 324,  
960 1–8. doi:10.1016/j.geoderma.2018.03.008

961 Sipos, P., Németh, T., Kis, V.K., Mohai, I., 2008. Sorption of copper, zinc and lead on soil  
962 mineral phases. *Chemosphere* 73, 461–469. doi:10.1016/j.chemosphere.2008.06.046

963 Slomberg, D.L., Ollivier, P., Radakovitch, O., Baran, N., Sani-Kast, N., Miche, H., Borschneck,  
964 D., Grauby, O., Bruchet, A., Scheringer, M., Labille, J., 2016. Characterisation of  
965 suspended particulate matter in the Rhone River: insights into analogue selection. *Environ.*  
966 *Chem.* doi:10.1071/EN15065

967 Sondi, I., Bišćan, J., Pravdić, V., 1996. Electrokinetics of pure clay minerals revisited. *J. Colloid*  
968 *Interface Sci.* 178, 514–522. doi:10.1006/jcis.1996.0146

969 Stumm, W., 1993. Aquatic colloids as chemical reactants: surface structure and reactivity.  
970 *Colloids Surfaces A Physicochem. Eng. Asp.* 73, 1–18. doi:10.1016/0927-  
971 7757(93)80003-W

972 Superville, P.J., Louis, Y., Billon, G., Prygiel, J., Omanović, D., Pižeta, I., 2011. An adaptable  
973 automatic trace metal monitoring system for on line measuring in natural waters. *Talanta*  
974 87, 85–92. doi:10.1016/j.talanta.2011.09.045

975 Tertre, E., Beaucaire, C., Coreau, N., Juery, A., 2009. Modelling Zn(II) sorption onto clayey  
976 sediments using a multi-site ion-exchange model. *Appl. Geochemistry* 24, 1852–1861.  
977 doi:10.1016/j.apgeochem.2009.06.006

978 Thomas, F., Michot, L.J., Vantelon, D., Montargès, E., Prélot, B., Cruchaudet, M., Delon, J.F.,

979 1999. Layer charge and electrophoretic mobility of smectites, in: Colloids and Surfaces  
980 A: Physicochemical and Engineering Aspects. pp. 351–358. doi:10.1016/S0927-  
981 7757(99)00291-5

982 Toner, B., Manceau, A., Webb, S.M., Sposito, G., 2006. Zinc sorption to biogenic hexagonal-  
983 birnessite particles within a hydrated bacterial biofilm. *Geochim. Cosmochim. Acta* 70,  
984 27–43. doi:10.1016/j.gca.2005.08.029

985 Trivedi, P., Axe, L., Dyer, J., 2001a. Adsorption of metal ions onto goethite: Single-adsorbate  
986 and competitive systems. *Colloids Surfaces A Physicochem. Eng. Asp.* 191, 107–121.  
987 doi:10.1016/S0927-7757(01)00768-3

988 Trivedi, P., Axe, L., Tyson, T. a., 2001b. An Analysis of Zinc Sorption to Amorphous versus  
989 Crystalline Iron Oxides Using XAS. *J. Colloid Interface Sci.* 244, 230–238.  
990 doi:10.1006/jcis.2001.7971

991 Trivedi, P., Dyer, J.A., Sparks, D.L., Pandya, K., 2004. Mechanistic and thermodynamic  
992 interpretations of zinc sorption onto ferrihydrite. *J. Colloid Interface Sci.*  
993 doi:10.1016/S0021-9797(03)00586-1

994 Viers, J., Dupré, B., Gaillardet, J., 2009. Chemical composition of suspended sediments in  
995 World Rivers: New insights from a new database. *Sci. Total Environ.* 407, 853–868.  
996 doi:10.1016/j.scitotenv.2008.09.053

997 Voegelin, A., Scheinost, A.C., Bühlmann, K., Barmettler, K., Kretzschmar, R., 2002. Slow  
998 formation and dissolution of Zn precipitates in soil: A combined column-transport and  
999 XAFS study. *Environ. Sci. Technol.* 36, 3749–3754. doi:10.1021/es010316m

1000 Wang, F., Chen, J., Forsling, W., 1997. Modeling sorption of trace metals on natural sediments  
1001 by surface complexation model. *Environ. Sci. Technol.* 31, 448–453.  
1002 doi:10.1021/es960270a

1003 Waychunas, G.A., Fuller, C.C., Davis, J.A., 2002. Surface complexation and precipitate

1004 geometry for aqueous Zn(II) sorption on ferrihydrite I: X-ray absorption extended fine  
1005 structure spectroscopy analysis. *Geochim. Cosmochim. Acta* 66, 1119–1137.  
1006 doi:10.1016/S0016-7037(01)00853-5

1007 Waychunas, G.A., Fuller, C.C., Davis, J.A., Rehr, J.J., 2003. Surface complexation and  
1008 precipitate geometry for aqueous Zn(II) sorption on ferrihydrite: II. XANES analysis and  
1009 simulation. *Geochim. Cosmochim. Acta* 67, 1031–1043. doi:10.1016/S0016-  
1010 7037(02)01280-2

1011 Yin, N.H., Sivry, Y., Benedetti, M.F., Lens, P.N.L., van Hullebusch, E.D., 2015. Application  
1012 of Zn isotopes in environmental impact assessment of Zn-Pb metallurgical industries: A  
1013 mini review. *Appl. Geochemistry* 64, 128–135. doi:10.1016/j.apgeochem.2015.09.016

1014 Young, L.B., Harvey, H.H., 1992. The relative importance of manganese and iron oxides and  
1015 organic matter in the sorption of trace metals by surficial lake sediments. *Geochim.  
1016 Cosmochim. Acta* 56, 1175–1186. doi:10.1016/0016-7037(92)90055-N

1017 Zhuang, J., Yu, G.R., 2002. Effects of surface coatings on electrochemical properties and  
1018 contaminant sorption of clay minerals. *Chemosphere* 49, 619–628. doi:10.1016/S0045-  
1019 6535(02)00332-6

1020 Zimmermann-Timm, H., 2002. Characteristics, Dynamics and Importance of Aggregates in  
1021 Rivers - An Invited Review. *Int. Rev. Hydrobiol.* 87, 197–240. doi:10.1002/1522-  
1022 2632(200205)87:2/3<197::AID-IROH197>3.0.CO;2-7

1023

1024

1025 **TABLE CAPTIONS**

1026

1027 *Table 1. CEC, textural properties for the different SPM and pure minerals, organic matter content and*  
 1028 *sampling details. CEC (mEq per 100 g) was measured from the adsorption of cobalt-hexamine. Sample*  
 1029 *names refer to the stations (PSV, FRO, MIL, PAM, ARG, FLO and THI) on the Moselle River and its*  
 1030 *tributaries. The stations are classified from upstream to downstream, PSV being the most upstream station*  
 1031 *within the Moselle watershed. See Le Meur et al. 2016 for details about the stations. Textural properties of*  
 1032 *SPM and model minerals, obtained by nitrogen adsorption measurements. N<sub>2</sub> surface area (SSA-BET, m<sup>2</sup> g<sup>-1</sup>,*  
 1033 *BET theory), energetic constant C; \* from Prelot 2001. Organic matter content was estimated from*  
 1034 *thermogravimetric curves (see Le Meur et al. 2017). The last column precises the sampled river and the*  
 1035 *mean dialy water flow at the day of SPM sampling (m<sup>3</sup> s<sup>-1</sup>). NM: not measured. NA: not applicable.*

1036

1037 *Table 2 - XANES fitting parameters, linear combinations of reference spectra. FRO-Jul13 and FRO-Dec12*  
 1038 *SPM samples before and after Zn adsorption. The suffix « Zni » refers to the different points of the adsorption*  
 1039 *curves on figure 2, and the 3k suffix means that the batch experiments were conducted with higher ionic*  
 1040 *strength in solution, electrical conductivity was set to 3000 μS cm<sup>-1</sup> by addition of NaNO<sub>3</sub> solution (1.2 M).*  
 1041 *N: number of reference spectra used for fitting, **SPM**: spectrum of the pristine SPM sample ; **Zn<sub>low</sub>-illite**: Zn*  
 1042 *adsorbed onto illite, low loading; **Zn<sub>high</sub>-illite**: Zn adsorbed onto illite, High loading; **Smec**: zinciferous*  
 1043 *smectite; **Zn<sub>low</sub>-calcite**: Zn adsorbed onto calcite, low loading; **Zn high calcite**: Zn adsorbed onto calcite,*  
 1044 *high loading; **Zncit**: Zn in aqueous solution, complexed with citrate; **Zn<sub>high</sub>-Goet**: Zn adsorbed onto goethite,*  
 1045 *high loading; **Zn<sub>high</sub>-FeH**: Zn adsorbed onto ferrihydrite, high loading; **ZnHDL**: Layered double hydroxide;*  
 1046 ***R<sub>x</sub> factor**, multiplied by 10<sup>4</sup>, **χ<sup>2</sup>** multiplied by 10<sup>2</sup>, **Red χ<sup>2</sup>** multiplied by 10<sup>4</sup> ; **[Zn]** : amount of adsorbed Zn,*  
 1047 *mmol kg<sup>-1</sup>.*

1048

1049 *Table 3. Zn adsorbed onto SPM, EXAFS fitting parameters, linear combinations of reference spectra.*  
 1050 *N : number of reference spectra used for fitting, **SPM**: spectrum of the pristine SPM sample ; **Zn<sub>low</sub>-illite**:*  
 1051 *Zn adsorbed onto illite, low loading; **Zn<sub>high</sub>-illite**: Zn adsorbed onto illite, High loading; **Zn<sub>low</sub>-calcite**: Zn*  
 1052 *adsorbed onto calcite, low loading; **Zn<sub>high</sub>-calcite**: Zn adsorbed onto calcite, high loading; **Zn<sub>high</sub>-FeH** : Zn*  
 1053 *adsorbed onto ferrihydrite, high loading; **ZnHDL**: Layered double hydroxide; **ZnO**: zincite ; **R<sub>x</sub> factor**,*  
 1054 *multiplied by 10<sup>2</sup>, **χ<sup>2</sup>**; **Red χ<sup>2</sup>**; **[Zn]**: Zn content or amount of adsorbed Zn, mmol kg<sup>-1</sup>.*

1055

1056 *Table 4. FRO-JUL 13 - EXAFS fitting parameters, shell by shell fitting using theoretical backscattering*  
 1057 *curves for the SPM sample FRO-Jul13 and derivatives obtained after Zn sorption. Summary of the local*  
 1058 *structural parameters derived from EXAFS data analysis (shell by shell fitting). The Zn EXAFS data were Fourier*  
 1059 *transformed over the k range Δk and fitted over the ΔR range with single scattering paths involving O, Zn or Al*  
 1060 *atoms. The amplitude reduction factor S<sub>0</sub><sup>2</sup> was fixed to 0.7 but the energy shift was released for fitting. The number*  
 1061 *of atoms of the first coordination shell was fixed to 6, excepted for the first sample FRO-Jul13. The number of*  
 1062 *atoms, the distance R and disorder σ<sup>2</sup> were released for all the coordination shells. Parameters with strong*  
 1063 *correlation factors were not released simultaneously.*

1064

1065 *Table 5. FRO-DEC 12 - EXAFS fitting parameters, shell by shell fitting using theoretical backscattering*  
1066 *curves for the SPM sample FRO-Jul13 and derivatives obtained after Zn sorption. Summary of the local*  
1067 *structural parameters derived from EXAFS data analysis (shell by shell fitting). The Zn EXAFS data were Fourier*  
1068 *transformed over the  $k$  range  $\Delta k$  and fitted over the  $\Delta R$  range with single scattering paths involving O, Zn or Al*  
1069 *atoms. The amplitude reduction factor  $S_0^2$  was fixed to 0.7 but the energy shift was released for fitting. The number*  
1070 *of atoms of the first coordination shell was fixed to 6, excepted for the first sample FRO-Jul13. The number of*  
1071 *atoms, the distance  $R$  and disorder  $\sigma^2$  were released for all the coordination shells. Parameters with strong*  
1072 *correlation factors were not released simultaneously.*

1073

1074

1075



1076 **FIGURE CAPTIONS**

1077 *Figure 1. Electrophoretic mobility measured for illite, ferrihydrite (FeH) and two Moselle River SPM*  
1078 *samples*

1079 *Figure 2. Batch experiments of Zn adsorption onto model minerals (A) and onto river SPM samples (B*  
1080 *and C). The third graph compares Zn adsorption on SPM using two different ionic strengths,*  
1081 *respectively set at 300 and 3000  $\mu\text{S cm}^{-1}$ .*

1082  
1083 *Figure 3. XANES spectra at Zn-K edge for model compounds and for FRO-Jul13 and FRO-Dec12*  
1084 *before and after Zn adsorption.*

1085 ***Left graph, model compounds***

1086 *(a) Zn smectite, sauconite, provided by Stephan Kaufhold (Kaufhold et al., 2015);*

1087 *(b) Illite du Puy, purified and size fractionated, Zn content 3.4 mmol kg<sup>-1</sup>;*

1088 *(c) Zn<sub>low</sub>-illite, Zn adsorbed onto illite, low Zn loading 5.8 mmol kg<sup>-1</sup>;*

1089 *(d) Zn<sub>low</sub>-illite-FeH, Zn adsorbed onto illite-FeH, low Zn loading 2.3 mmol kg<sup>-1</sup>;*

1090 *(e) Zn<sub>high</sub>-illite, Zn adsorbed onto illite, high Zn loading 89 mmol kg<sup>-1</sup>;*

1091 *(f) Zn<sub>high</sub>-illite-FeH, Zn adsorbed onto illite-FeH, high Zn loading 75 mmol kg<sup>-1</sup>;*

1092 *(g) Zn<sub>high</sub>-Goethite, Zn adsorbed onto Goethite, Zn loading 58 mmol kg<sup>-1</sup>;*

1093 *(h) Zn<sub>high</sub>-FeH, Zn adsorbed onto ferrihydrite, high Zn loading 57 mmol kg<sup>-1</sup>.*

1094 *(i) Zn<sub>low</sub>-calcite, Zn adsorbed onto Calcite, low Zn loading 2 mmol kg<sup>-1</sup>;*

1095 *(j) Zn<sub>high</sub>-calcite, Zn precipitated onto calcite, Zn:Ca ratio 0.16:1.*

1096 *(k) Zn double layer hydroxide provided by Valerie Briois (Roussel et al., 2001; Carvalho et al., 2013)*

1097 *(l) Zn citrate in solution.*

1098 ***Middle graph***

1099 *(a) FRO-Jul13, Zn content 4.6 mmol kg<sup>-1</sup>; (b) Zn1, adsorbed Zn 4.1 mmol kg<sup>-1</sup>; (c) Zn2, adsorbed Zn*

1100 *20.5 mmol kg<sup>-1</sup>; (d) Zn3, adsorbed Zn 28.2 mmol kg<sup>-1</sup>; (e) Zn7, adsorbed Zn 159 mmol kg<sup>-1</sup>; (f) Zn10,*

1101 *adsorbed Zn 257.5 mmol kg<sup>-1</sup>; (g) Zn5-3k, adsorbed Zn 74.3 mmol kg<sup>-1</sup>; (h) Zn7-3k, adsorbed Zn 119.2*

1102 *mmol kg<sup>-1</sup>; (i) Zn10-3k, adsorbed Zn 205 mmol kg<sup>-1</sup>. –*

1103 ***Right graph***

1104 *(a) FRO-Dec12 Zn content 4 mmol kg<sup>-1</sup>; (b) Zn1, adsorbed Zn 4.2 mmol kg<sup>-1</sup>; (c) Zn2, adsorbed Zn 16.2*

1105 *mmol kg<sup>-1</sup>; (d) Zn7, adsorbed Zn 138 mmol kg<sup>-1</sup>; (e) Zn10, adsorbed Zn 214 mmol kg<sup>-1</sup>; (f) Zn5-3k,*

1106 *adsorbed Zn 71.7 mmol kg<sup>-1</sup>; (g) Zn7-3k, adsorbed Zn 117.6 mmol kg<sup>-1</sup>. The suffix “-3k” refers to Zn*

1107 *adsorption experiments performed with higher ionic strength, i.e., electric conductivity was set to 3000*

1108  *$\mu\text{S cm}^{-1}$  instead of 300  $\mu\text{S cm}^{-1}$ .*

1109

1110 *Figure 4: EXAFS Oscillations  $k^3 \chi(k)$  for reference samples. (a) zincite; (b) Zn smectite-sauconite; (c)*  
1111 *illite, Zn content 220 mg kg<sup>-1</sup>; (d) Zn<sub>low</sub>-illite, Zn adsorbed onto illite, low Zn loading 3 mmol kg<sup>-1</sup>; (e)*  
1112 *Zn<sub>high</sub>-illite, Zn adsorbed onto illite, high Zn loading 89 mmol kg<sup>-1</sup>; (f) Zn<sub>low</sub>-calcite, Zn adsorbed onto*  
1113 *Calcite, low Zn loading 2 mmol kg<sup>-1</sup>; (g) Zn<sub>high</sub>-calcite, Zn precipitated onto calcite, Zn:Ca ratio 0.16:1;*  
1114 *(h) Zn<sub>high</sub>-FeH, Zn adsorbed onto ferrihydrite, high Zn loading 57 mmol kg<sup>-1</sup>; (i) Zn citrate in aqueous*  
1115 *solution; (j) Zn double layer hydroxide provided by Valerie Briois (Roussel et al., 2001; Carvalho et*  
1116 *al., 2013); (k) amorphous ZnS.*

1117

1118 *Figure 5. EXAFS and corresponding Fourier transform (magnitude and imaginary parts) for FRO-*  
1119 *Jul13 before and after Zn adsorption. Experimental curves and Linear Combination fitting curves – (a)*  
1120 *FRO-Jul13; (b) FRO-Jul13 Zn1; (c) FRO-Jul13 Zn2; (d) FRO-Jul13 Zn3; (e) FRO-Jul13 Zn7; (f) FRO-*  
1121 *Jul13 Zn10.*

1122

1123 *Figure 6. EXAFS and corresponding Fourier transform (magnitude and imaginary parts) FRO-Dec12*  
1124 *before and after Zn adsorption. Experimental and Linear Combination Fitting curves – (a) FRO-Dec12;*  
1125 *(b) FRO-Dec12 Zn2; (c) FRO-Dec12 Zn7; (d) FRO-Dec12 Zn10.*

1126

1127 *Figure 7: Shell by shell fitting, Zn adsorbed onto SPM FRO-Jul13. Experimental (black full line) and*  
1128 *theoretical (red dashed line) EXAFS oscillations  $k^3 \chi(k)$  and Fourier Transform (amplitude and*  
1129 *imaginary parts) for FROjul13 before and after Zn adsorption with increasing Zn loading: (a) FRO-*  
1130 *Jul13, (b) FRO-Jul13 Zn1, (c) FRO-Jul13 Zn2, (d) FRO-Jul13 Zn3, (e) FRO-Jul13 Zn7, (f) FRO-Jul13*  
1131 *Zn10.*

1132

1133 *Figure 8: Shell by shell fitting, Zn adsorbed onto SPM FRO-Dec12. Experimental (black full line) and*  
1134 *Theoretical (red dashed line) EXAFS oscillations  $k^3 \chi(k)$  and Fourier Transform (amplitude and*  
1135 *imaginary parts) for FRO-Dec12 before and after Zn adsorption with increasing Zn loading: (a) FRO-*  
1136 *Dec12, (b) FRO-Dec12 Zn2, (c) FRO-Dec12 Zn7, (d) FRO-Dec12 Zn10.*

1137

1138

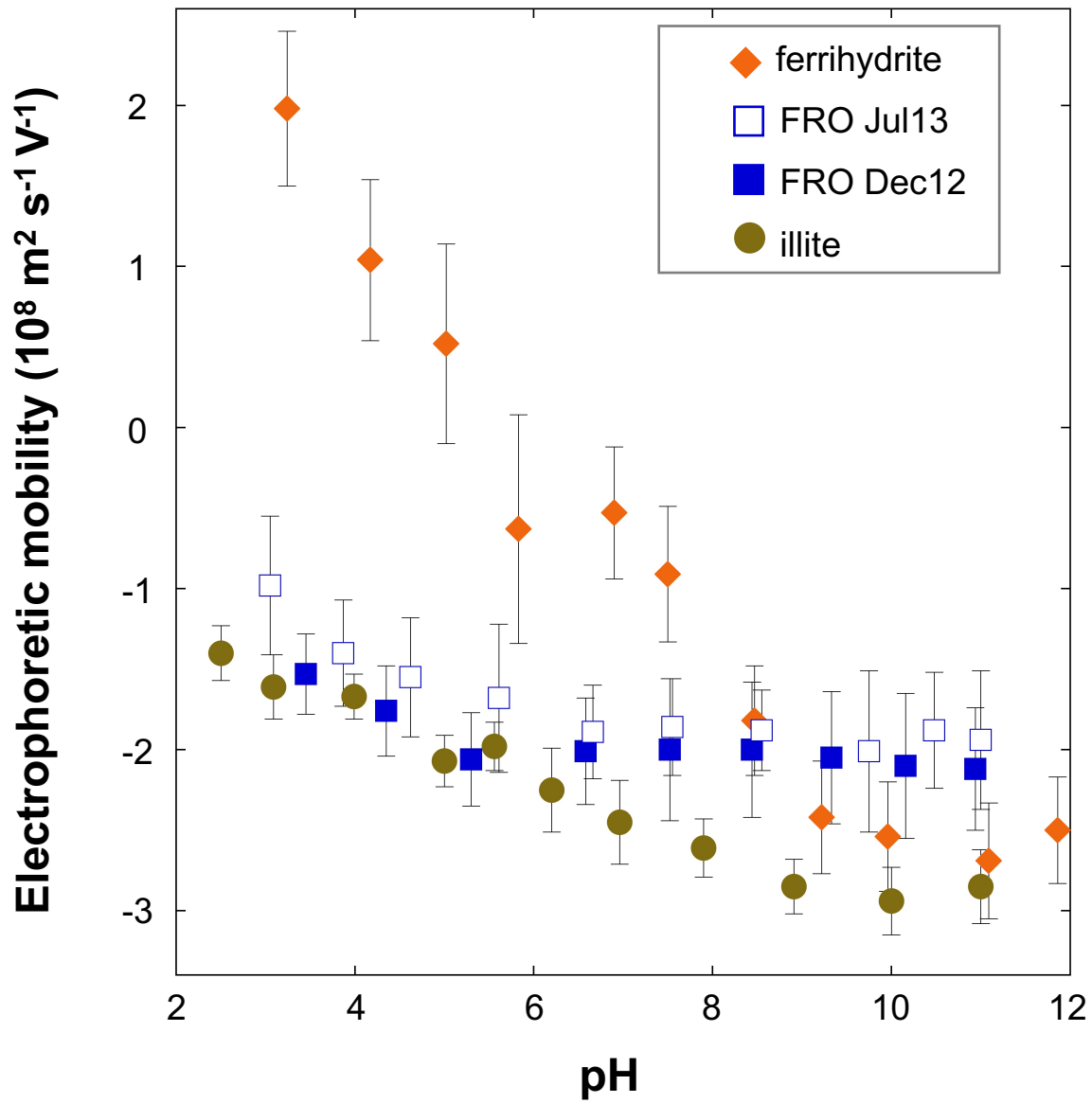


figure 1

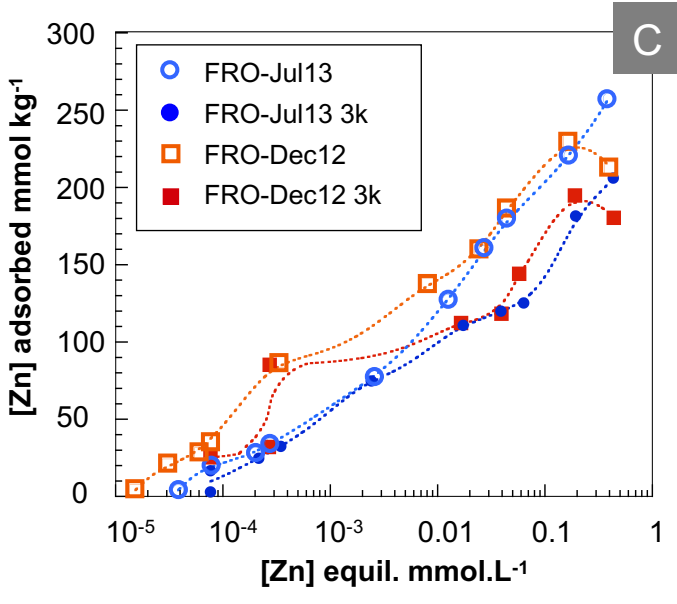
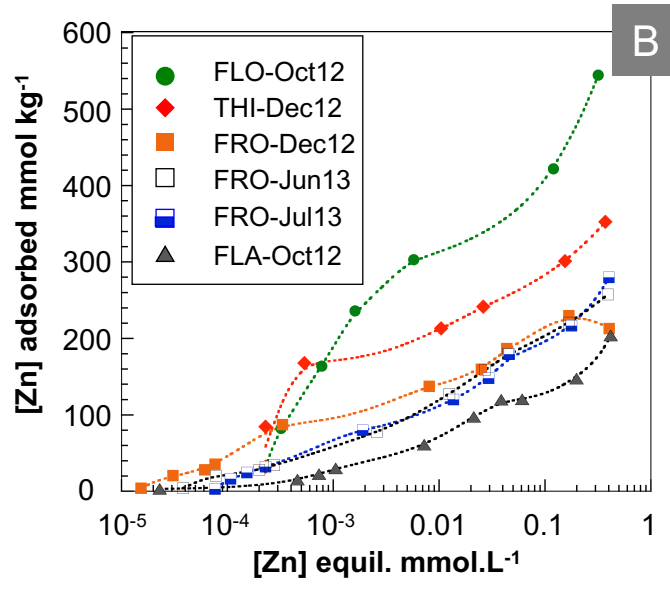
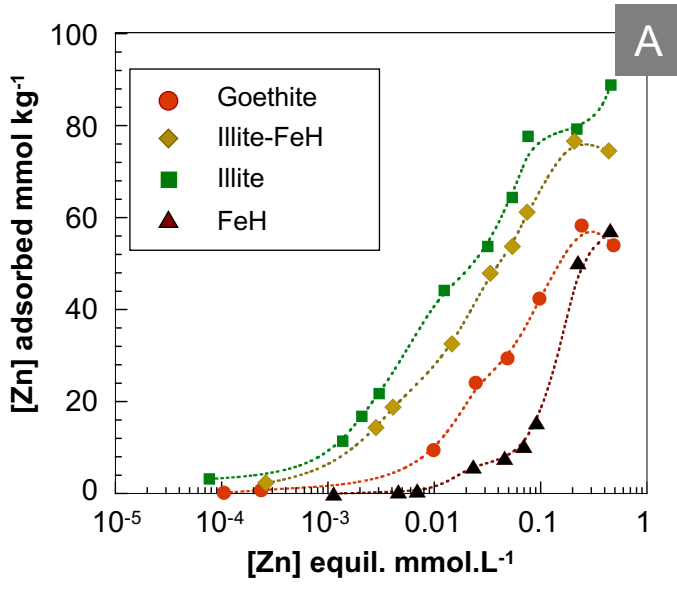


figure 2

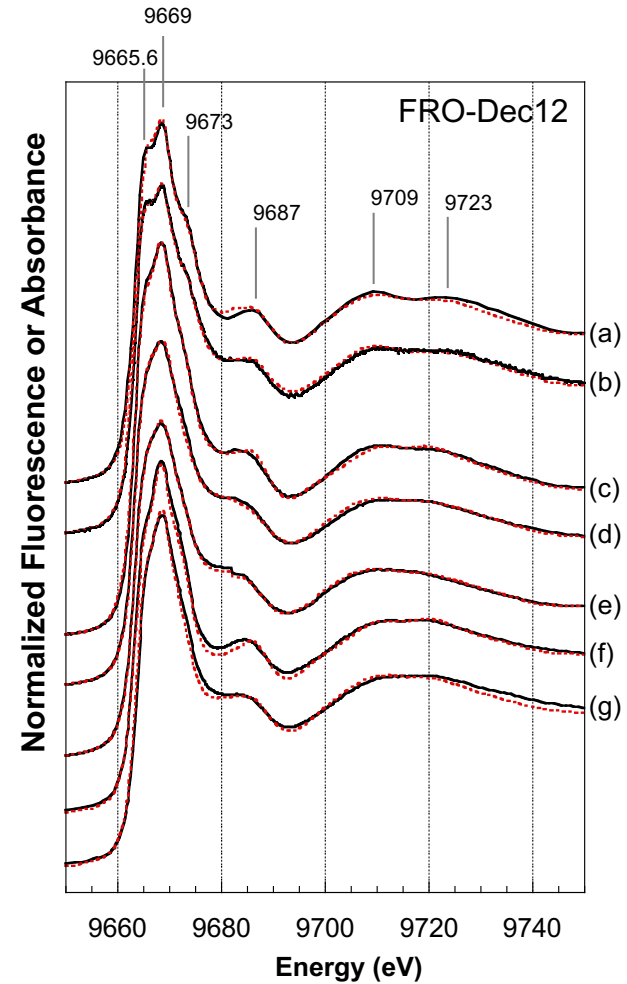
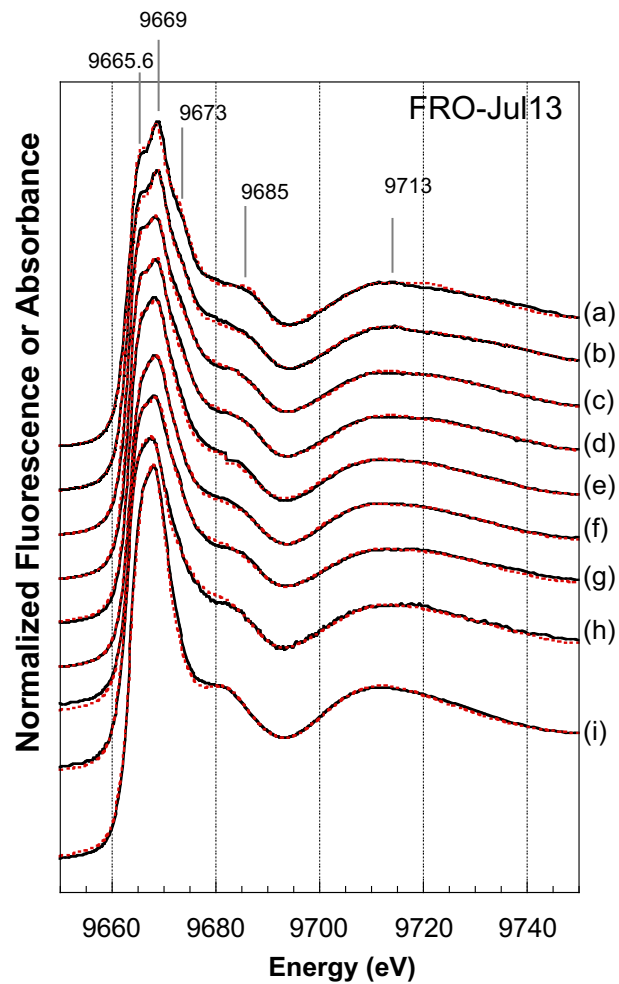
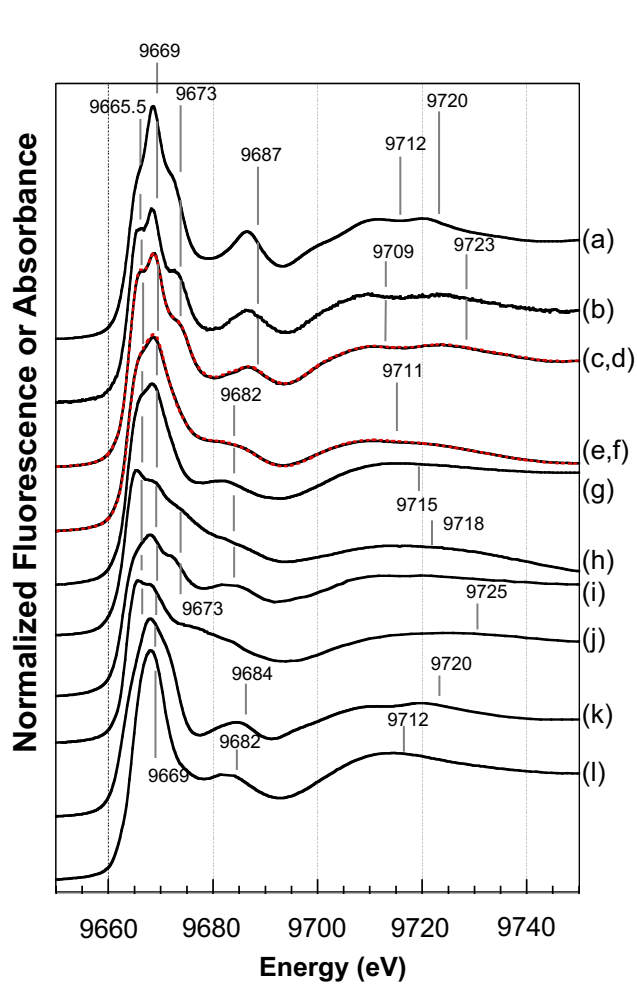


figure 3

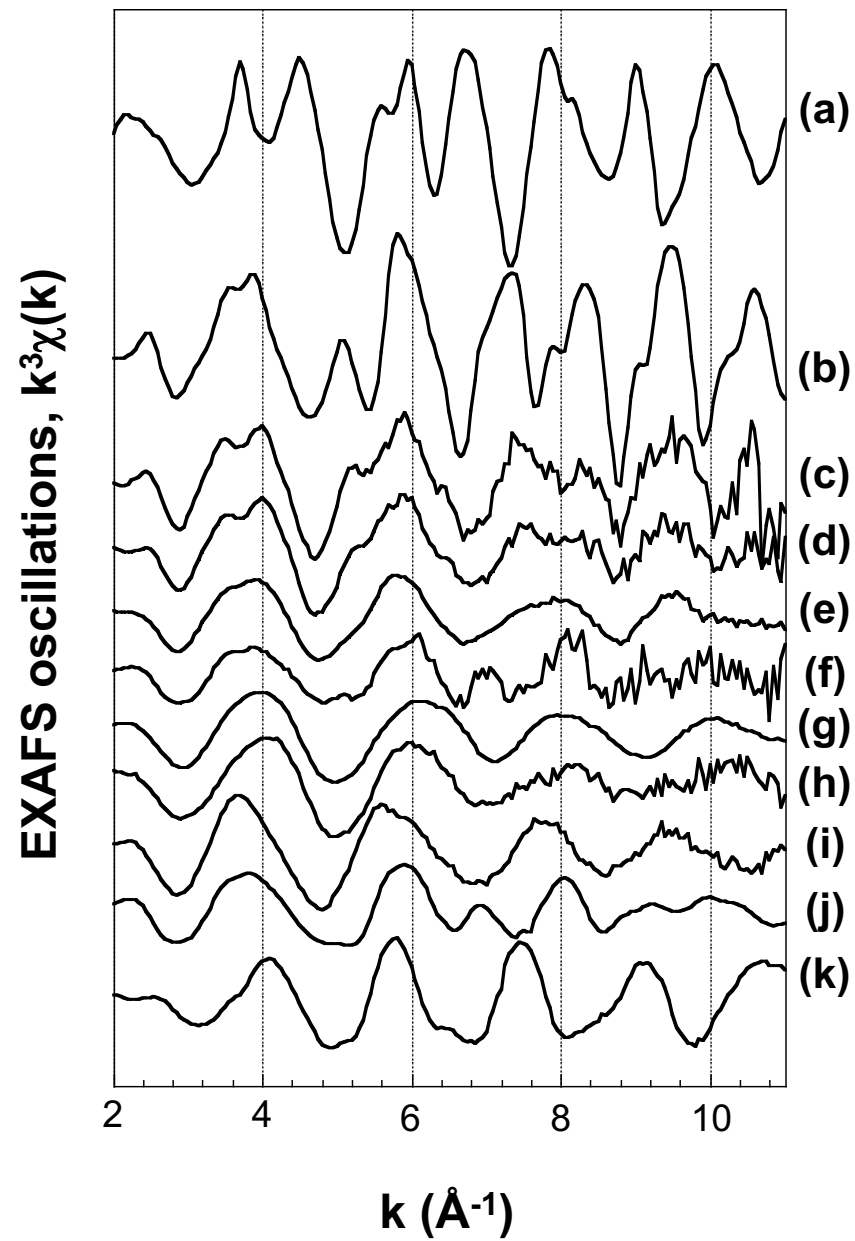


figure 4

figure 5

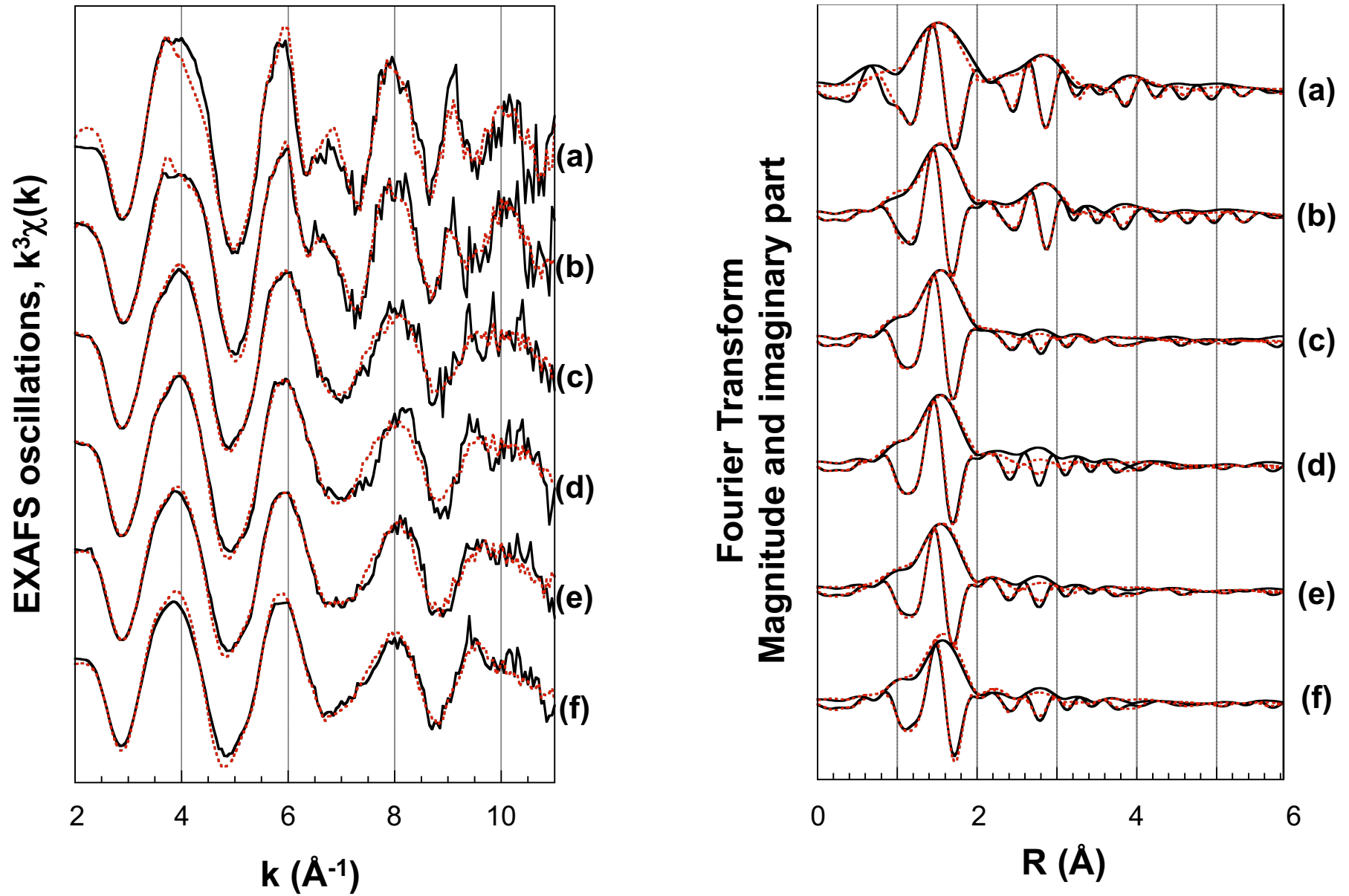


figure 6

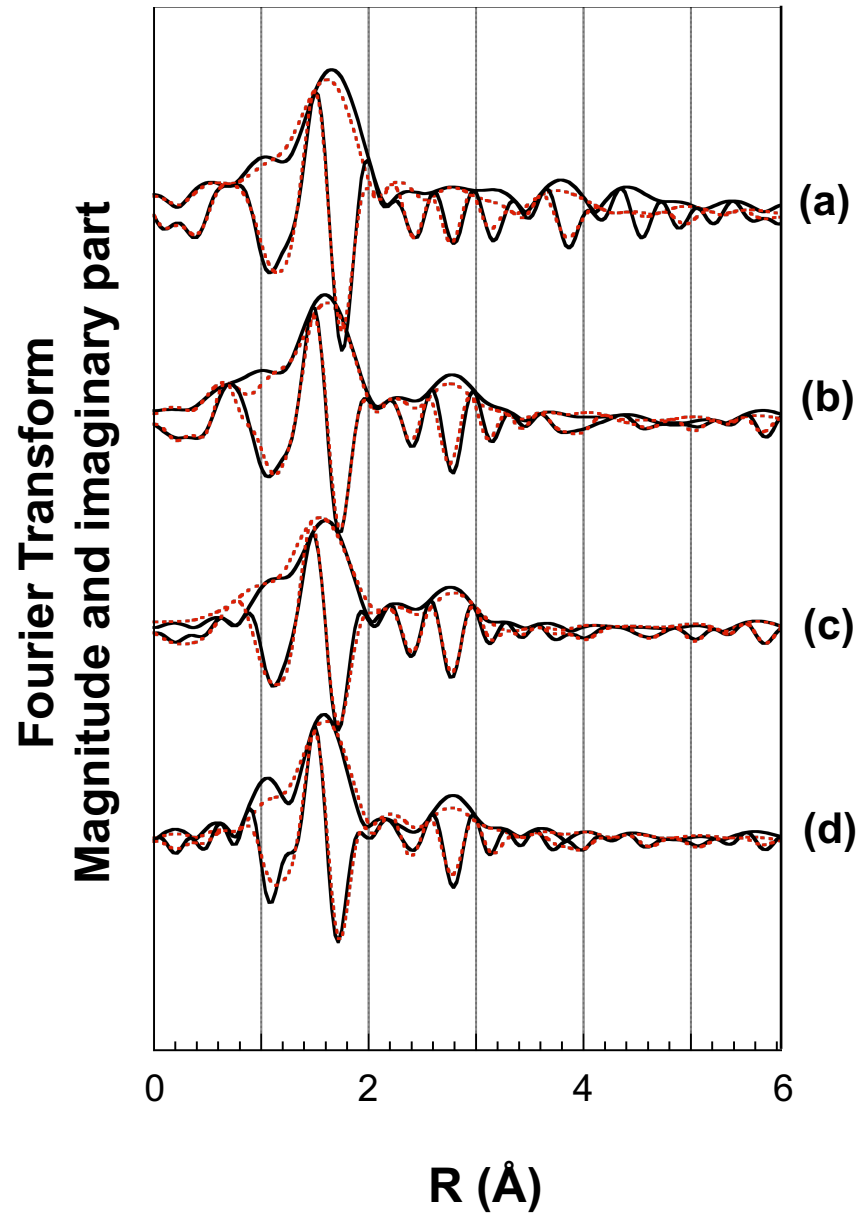
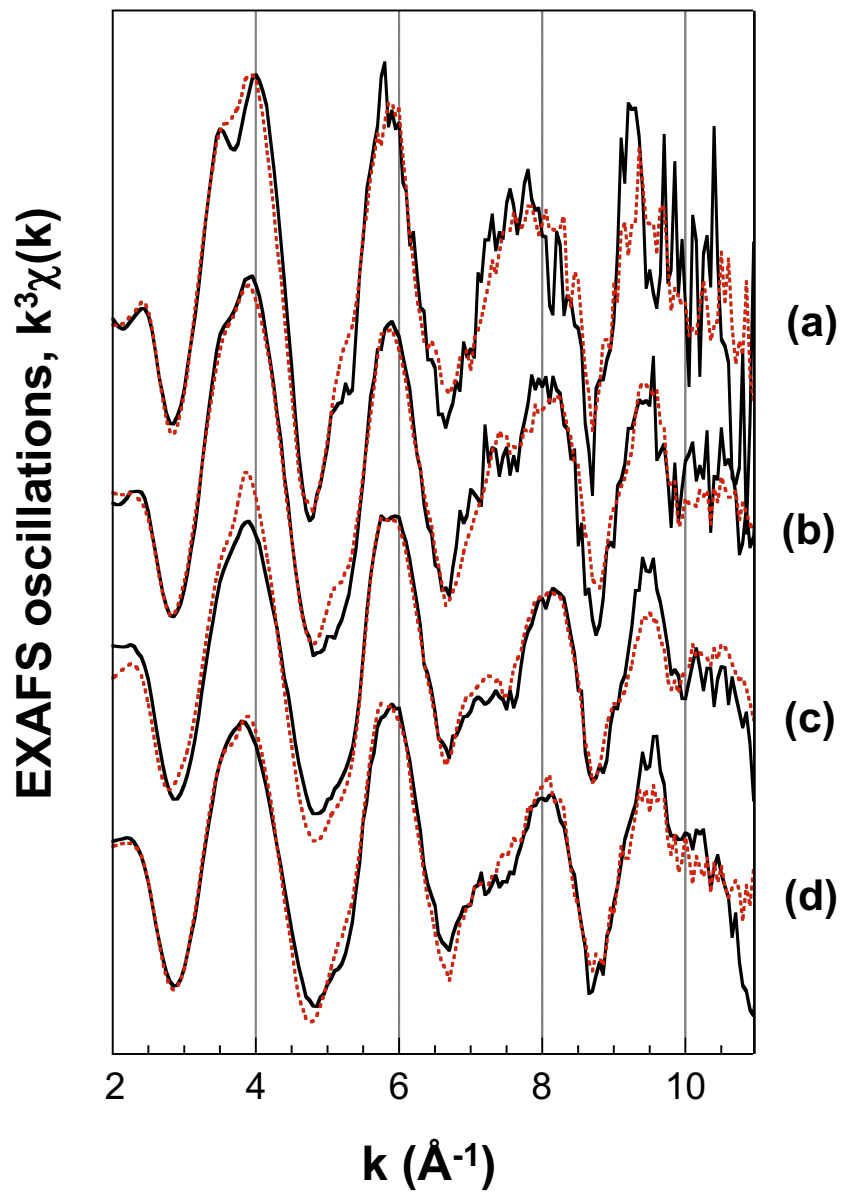




figure 7

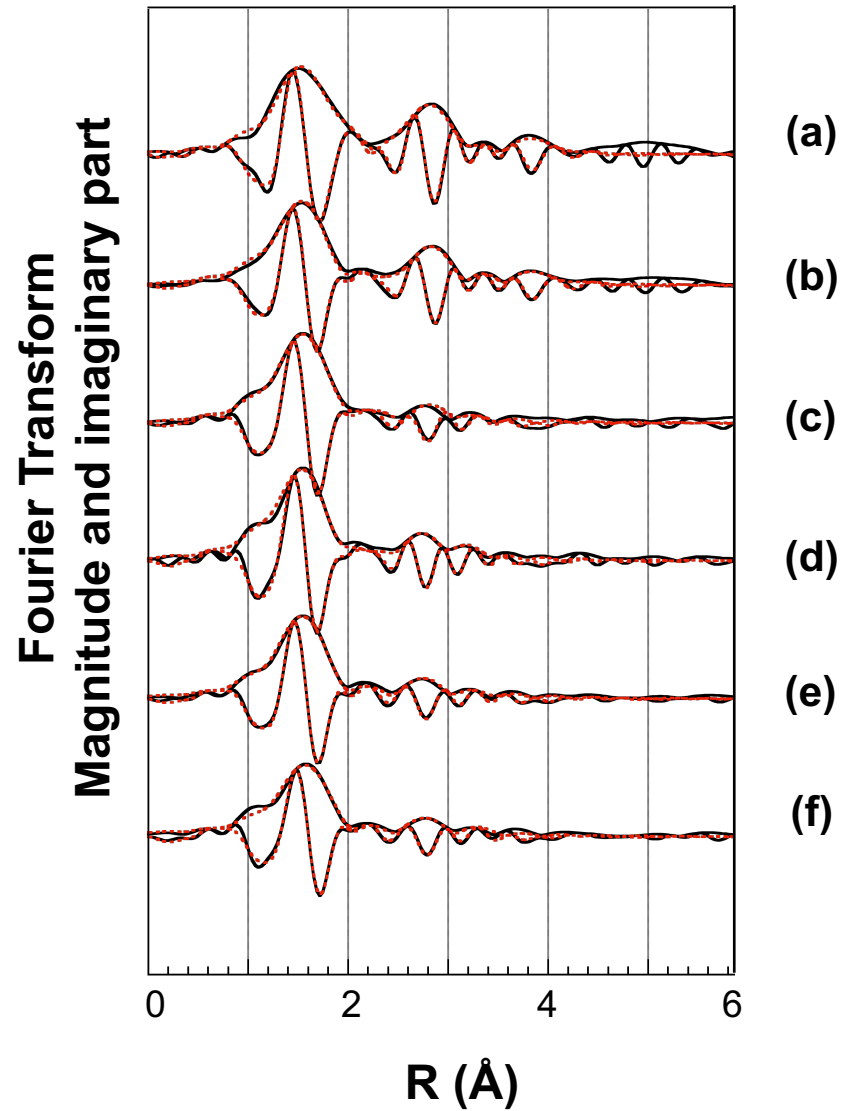
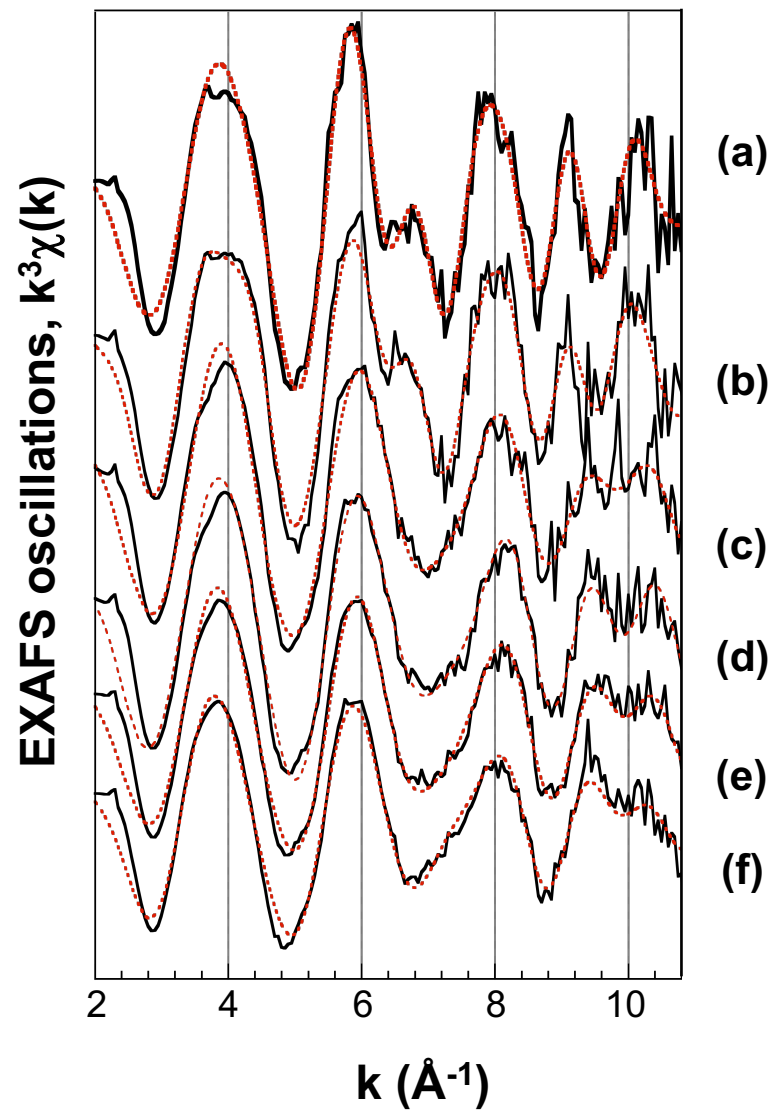


Table 1. CEC, textural properties for the different SPM samples and pure minerals, organic matter content and sampling details. CEC (mEq per 100 g) was measured from the adsorption of cobalt-hexamine. Sample names refer to the stations (PSV, FRO, MIL, PAM, ARG, FLO and THI) on the Moselle River and its tributaries. The stations are classified from upstream to downstream, PSV being the most upstream station within the Moselle watershed. See Le Meur et al. 2016 for details about the stations. Textural properties of SPM and model minerals, obtained by nitrogen adsorption measurements. N<sub>2</sub> surface area (SSA-BET, m<sup>2</sup> g<sup>-1</sup>, BET theory), energetic constant C; \* from Prelot 2001. Organic matter content was estimated from thermogravimetric curves (see Le Meur et al. 2017). The last column precises the sampled river and the mean daily water flow at the day of SPM sampling (m<sup>3</sup> s<sup>-1</sup>). NM: not measured. NA: not applicable. FRO samples are classified as a function of organic matter content.

sample	CEC mean value (meq per 100 g)	SSA-BET (m <sup>2</sup> g <sup>-1</sup> )	C, energetic constant	microporous surface (m <sup>2</sup> g <sup>-1</sup> )	Organic matter content %	River and Qmd water flow
FeH	NM	218	172	47.6	0	NA
Illite T3	20.3	155	177	28	0	NA
illite-FeH	NM	124	151	28.5	0	NA
Goethite*	NM	18	NA	0	0	NA
FLA-Nov12	NM	15.5	129	1.15	10.8	Moselle 70
PSV-Dec12	42.8	35.5	104	1.1	5.1	Madon 27
PSV-Nov12	28.9	37	114	1.1	5.9	Madon 7
FRO-Dec12	39	31.9	85	Non micr.	5.0	Moselle 397
FRO-Feb14	38.3	32	95	1.2	5.6	Moselle 124
FRO-Nov12	35.2	32.3	66	Non micr.	7.0	Moselle 82
FRO-Jun13	43.6	24.4	70	Non micr.	7.6	Moselle 35
FRO-Jul13	46.7	17.2	85	0.8	8	Moselle 15
MIL-Nov12	31.7	NM	NM	NM	NM	Moselle 233
PAM-Feb13	33.9	32.9	118	1.3	5.2	Moselle 156
PAM-Nov12	42.0	24.4	70	Non micr.	7.5	Moselle 81
ARG-Nov12	40.4	22.9	94	1.0	NM	Moselle 185
FLO-Oct12	37.4	7.4	49	Non micr.	17.4	Fensch 0.6
THI-Dec12	41.6	28	88	Non micr.	6.0	Moselle 200

TABLE 2 - XANES fitting parameters, linear combinations of reference spectra.

**XANES spectra fitting, FRO-Jul13 and FRO-Dec12 SPM samples before and after Zn adsorption.** The suffix « Zni » refers to the different points of the adsorption curves on figure 2, and the 3k suffix means that the batch experiments were conducted with higher ionic strength in solution, electrical conductivity was set to 3000  $\mu\text{S}\cdot\text{cm}^{-1}$  by addition of  $\text{NaNO}_3$  solution (1.2 M).

**N:** number of reference spectra used for fitting, **SPM:** spectrum of the pristine SPM sample ; **Zn<sub>low</sub>-illite:** Zn sorbed onto illite, low loading; **Zn<sub>high</sub>-illite:** Zn sorbed onto illite, High loading; **Smec:** zinciferous smectite; **Zn<sub>low</sub>-calcite:** Zn sorbed onto calcite, low loading; **Zn high calcite:** Zn sorbed onto calcite, high loading; **Zn<sub>low</sub>-apatite:** Zn sorbed onto apatite, low loading; **Zn<sub>high</sub>-apatite:** Zn sorbed onto apatite, high loading; **Zncit :** Zn in aqueous solution, complexed with citrate; **Zn<sub>high</sub>-Goet:** Zn sorbed onto goethite, high loading; **Zn<sub>high</sub>-FeH :** Zn sorbed onto ferrihydrite, high loading; **ZnHDL:** Layered double hydroxide; **ZnO:** zincite ; **R<sub>x</sub> factor,** multiplied by  $10^4$ ,  $\chi^2$  multiplied by  $10^2$ , **Red  $\chi^2$**  multiplied by  $10^4$  ; **[Zn]** : amount of sorbed Zn,  $\text{mmol}\cdot\text{kg}^{-1}$ .

Sample / Reference	N	SPM	Zn low illite	Zn high illite	Smec	Zn high calcite	Zn low calcite	Zn cit	Zn high Goet	Zn high FeH	Zn HDL	R <sub>x</sub> (*10 <sup>4</sup> )	$\chi^2$	Red $\chi^2$	[Zn]
a- FRO-Jul13	3			0.09	0.27					0.64		15.3	11.5	4.3	4.6
b- FRO-Jul13 Zn1	2	0.91				0.09						6.7	5.1	1.9	4.1
c- FRO-Jul13 Zn2	3	0.41						0.14		0.45		7.0	5.4	2.0	20.5
d- FRO-Jul13 Zn3	3	0.49						0.14		0.37		10	7.7	2.8	28.2
e- FRO-Jul13 Zn7	2			0.62						0.38		4.7	3.2	1.2	159.1
f- FRO-Jul13 Zn10	3			0.68				0.06		0.26		3	2.1	0.8	257.5
g- FRO-Jul13 Zn5-3k	3			0.37					0.25	0.38		21	11.5	3	74.3
h- FRO-Jul13 Zn7 3k	2							0.34		0.66		17	16	5	119.2
i- FRO-Jul13 Zn10 3k	2							0.39	0.61			21	26	7	204.9
a-FROdec12	2		0.54				0.46					29.1	19.4	12	4.0
b- FRO-Dec12 Zn1	2	0.73					0.27					18	21	3.6	2.9
c- FRO-Dec12 Zn2	3				0.30					0.52	0.18	8.6	7.3	2.7	16.2
d- FRO-Dec12 Zn7	2			0.69			0.12			0.19		4.4	3.0	1.0	137.8
e- FRO-Dec12 Zn10	2			0.71			0.29					6	3.5	1	214.2
f- FRO-Dec12 Zn5-3k	3				0.38					0.33	0.29	60	34	10	71.7
g- FRO-Dec12 Zn7-3k	3		0.29	0.44							0.27	70	44	13	117.6

Table 3. Zn adsorbed onto SPM samples, EXAFS fitting parameters, linear combinations of reference spectra.

**N** : number of reference spectra used for fitting, **SPM**: spectrum of the pristine SPM sample ; **Zn<sub>low</sub>-illite**: Zn sorbed onto illite, low loading; **Zn<sub>high</sub>-illite**: Zn sorbed onto illite, High loading; **Zn<sub>low</sub>-calcite**: Zn sorbed onto calcite, low loading; **Zn<sub>high</sub>-calcite**: Zn sorbed onto calcite, high loading; **Zn<sub>high</sub>-FeH** : Zn sorbed onto ferrihydrite, high loading; **ZnHDL**: Layered double hydroxide; **ZnO**: zincite ; **R<sub>x</sub> factor**, multiplied by 10<sup>2</sup>; **χ<sup>2</sup>**, **Red χ<sup>2</sup>**; **[Zn]**: amount of adsorbed Zn, mmol kg<sup>-1</sup>.

Sample / Reference	N	Zn low Illite	Zn high Illite	Zn high calcite	Zn low calcite	FeH ZnH	Zn HDL	ZnO	R <sub>E</sub> (*10 <sup>2</sup> )	χ <sup>2</sup>	Red χ <sup>2</sup>	[Zn]
<i>a- FRO-Jul13</i>	3	0.5				0.25		0.25	9.5	98	0.71	4.6
b- FRO-Jul13 Zn1	3		0.46			0.34		0.2	5.1	42	0.30	4.1
c- FRO-Jul13 Zn2	3		0.45	0.21		0.34			4.7	32	0.23	20.5
d- FRO-Jul13 Zn3	3		0.49	0.26		0.25			5.6	40	0.29	28.2
e- FRO-Jul13 Zn7	3		0.49	0.35	0.16				3	18	0.13	159.1
f- FRO-Jul13 Zn10	3		0.69	0.19			0.12		3.6	19	0.14S	257.5
<i>a- FRO-Dec12</i>	3	0.73					0.21	0.06	12.2	153	1.10	4.0
b- FRO-Dec12 Zn2	3		0.37			0.27	0.36		4.7	46	0.33	16.2
c- FRO-Dec12 Zn7	3			0.27		0.20	0.53		7.1	48	0.35	137.8
d- FRO-Dec12 Zn10	3		0.44	0.24			0.32		3.7	27	0.19	214.2

Table 4. FRO-JUL 13 - EXAFS fitting parameters, shell by shell fitting using theoretical backscattering curves for the SPM sample FRO-Jul13 and derivatives obtained after Zn sorption. Summary of the local structural parameters derived from EXAFS data analysis (shell by shell fitting). The Zn EXAFS data were Fourier transformed over the k range  $\Delta k$  and fitted over the  $\Delta R$  range with single scattering paths involving O, Zn or Al atoms. The amplitude reduction factor  $S_0^2$  was fixed to 0.7 but the energy shift was released for fitting. The number of atoms of the first coordination shell was fixed to 6, excepted for the first sample FRO-Jul13. The number of atoms, the distance R and disorder  $\sigma^2$  were released for all the coordination shells. Parameters with strong correlation factors were not released simultaneously.

	Fitting range $\Delta k(\text{\AA}^{-1})$	Fitting range $\Delta R(\text{\AA})$	shell	Number of atoms	R( $\text{\AA}$ )	$\sigma^2(\text{\AA}^2)$	$\Delta E(\text{eV})$	$S_0^2$	R factor
FRO-Jul13	2.8-10.9	1-4.3	Zn-O	5	1.99±0.01	0.007±0.001	-1.0 ± 0.2	0.70	0.0003
			Zn-S	0.9±0.2	2.32±0.01	0.004±0.002			
			Zn-Zn	3±1	3.18 ±0.02	0.012±0.0012			
			Zn-O	1.32±1	3.77 ±0.02	0.009±0.001			
			Zn-Zn	1±0.5	4.15±0.02	0.011±0.002			
			Zn-O	5±1	4.52±0.02	0.006±0.0015			
FRO-Jul13 Zn1	2.8-10.9	1-4.3	Zn-O	6.0	2.0±0.01	0.0098±0.001	0.5 ± 0.2	0.70	0.0002
			Zn-Zn	3.5	3.19±0.01	0.010±0.002			
			Zn-O	3.4±1	3.78±0.01	0.008±0.002			
			Zn-Zn	0.7±0.6	3.78±0.012	0.011±0.002			
			Zn-O	3.3±1	4.14±0.015	0.011±0.002			
FRO-Jul13 Zn2	2.8-10.9	1-3.5	Zn-O	6	2.0±0.005	0.01±0.001	1.7 ± 0.3	0.70	0.00007
			Zn-Zn	0.9±0.7	3.13±0.006	0.008±0.002			
			Zn-Al	2±1	3.62±0.02	0.013±0.002			
FRO-Jul13 Zn3	2.8-10.9	1-4.1	Zn-O	6	5.9	0.011±0.001	-0.5 ± 0.2	0.70	0.0007
			Zn-Zn	1±0.3	3.10±0.02	0.0048±0.0015			
			Zn-Al	1.4±0.5	3.58±0.02	0.0073±0.001			
FRO-Jul13 Zn7	2.8-10.9	1-3.9	Zn-O	6.0	2.01±0.01	0.009±0.001	-0.12 ± 0.2	0.7	0.0004
			Zn-Zn	1.0±0.3	3.10±0.01	0.0062±0.0005			
			Zn-O	2±0.5	3.66±0.01	0.008±0.001			
FRO-Jul13 Zn10	2.8-10.9	1-3.9	Zn-O	6.0	2.03±0.01	0.009±0.001	1.4 ± 0.1	0.70	0.0005
			Zn-Zn	1.2±0.3	3.122±0.01	0.0075±0.001			
			Zn-O	2±0.5	3.76±0.02	0.0075±0.005			

Table 5. FRO-DEC12 - EXAFS fitting parameters, shell by shell fitting using theoretical backscattering curves for the SPM sample FRO-Dec12 before and after Zn sorption. Summary of the local structural parameters derived from EXAFS data analysis (shell by shell fitting). The Zn EXAFS data were Fourier transformed over the k range  $\Delta k$  and fitted over the  $\Delta R$  range with single scattering paths involving O, Zn or Al atoms. The amplitude reduction factor  $S_0^2$  was fixed to 0.7 but the energy shift was released for fitting. The number of atoms of the first coordination shell was fixed to 6. The number of atoms, the distance R and disorder  $\sigma^2$  were released for all the coordination shells. Parameters with strong correlation factors were not released simultaneously.

	Fitting range $\Delta k(\text{\AA}^{-1})$	Fitting range $\Delta R(\text{\AA})$	shell	Number of atoms	R( $\text{\AA}$ )	$\sigma^2(\text{\AA}^2)$	$\Delta E(\text{eV})$	$S_0^2$	R factor
FRO-Dec12	2.8-10.6	1.25-4.3	Zn-O	6.0	2.09±0.01	0.009±0.0005	6.9 ± 0.2	0.70	0.0007
			Zn-Zn	1.4±0.7	3.14±0.02	0.006±0.0005			
			Zn-Al	2±0.8	3.13±0.04	0.01±0.001			
			Zn-Zn	1±0.3	3.89±0.01	0.008±0.001			
			Zn-O	6±2	4.00±0.01	0.009±0.001			
FRO-Dec12 Zn2	2.8-11	1-3.5	Zn-O	6.0	2.05±0.005	0.0815±0.005	3.7 ± 0.2	0.7	0.0003
			Zn-Zn	2±0.5	3.13±0.01	0.008±0.001			
			Zn-Zn	0.7±0.5	3.34±0.01	0.010±0.001			
			Zn-O	2	3.93±0.01	0.01±0.001			
FRO-Dec12 Zn7	2.9-11	1-3.9	Zn-O	6.0	2.03±0.005	0.009±0.001	1.6 ± 0.1	0.7	0.0005
			Zn-Zn	1.5±0.5	3.10±0.01	0.006±0.001			
			Zn-Zn	0.7±0.5	3.27±0.01	0.01±0.001			
FRO-Dec12 Zn10	2.9-11	1.2-3.8	Zn-O	6.0	2.04±0.01	0.009±0.001	1.6 ± 0.1	0.7	0.0003
			Zn-Zn	1.5±0.5	3.12±0.01	0.007±0.001			

figure 8

