



## Dynamics of copper and zinc sedimentation in a lagooning system receiving landfill leachate



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### ARTICLE INFO

#### Article history:

Received 1 December 2012

Accepted 4 June 2013

Available online 28 June 2013

#### Keywords:

Lagooning system

Sediment

Trace metals

Edge effect

Landfill

Leachate

### ABSTRACT

This study characterises the sediment dredged from a lagooning system composed of a settling pond and three lagoons that receive leachates from a municipal solid waste (MSW) landfill in France. Organic carbon, carbonate, iron oxyhydroxides, copper (Cu) and zinc (Zn) concentrations were measured in the sediment collected from upstream to downstream in the lagooning system. In order to complete our investigation of sedimentation mechanisms, leachates were sampled in both dry (spring) and wet (winter) seasonal conditions. Precipitation of calcite and amorphous Fe-oxyhydroxides and sedimentation of organic matter occurred in the settling pond. Since different distributions of Zn and Cu concentrations are measured in sediment samples collected downstream in the lagooning system, it is suggested that these elements were not distributed in a similar way in the leachate fractions during the first stage of treatment in the settling pond, so that their sedimentation dynamics in the lagooning system differ. In the lagoons, it was found that organic carbon plays a major role in Cu and Zn mobility and trapping. The presence of macrophytes along the edges provided an input of organic matter that enhanced Cu and Zn scavenging. This edge effect resulted in a two-fold increase in Cu and Zn concentrations in the sediment deposited near the banks of the lagoons, thus confirming the importance of vegetation for the retention of Cu and Zn in lagooning systems.

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### 1. Introduction

Landfilling is a common way to manage municipal solid waste (MSW) in many countries. Large amounts of pollutants accumulate in these dumping sites and can contaminate the environment (Kjeldsen et al., 2002). There are two migration paths for pollutants from landfill sites to the environment: gaseous emissions of volatile organic compounds (Chiriac et al., 2007), and outflow of waste leachates, rich in nutrients, trace metals and organic compounds (Christensen et al., 2001; Kjeldsen et al., 2002). The dissemination of such contaminated leachates into the environment is critical and therefore site monitoring has become a major concern for the authorities and the scientific community in recent decades.

Leachate is generated when infiltration of rainwater and/or surface runoff results in excess moisture in waste layers. Four groups of pollutants are identified in landfill leachate: dissolved organic matter (DOM), inorganic macrocomponents, trace metals and xenobiotic organic compounds (Christensen et al., 2001). For example, more than 90 organic and metal organic complexes and

50 inorganic compounds have been detected in leachates and sediments from 12 municipal landfill sites in Sweden (Öman and Junestedt, 2008). Leachate composition changes over time, with both short- and long-term variations; it is also affected by the amount of waste deposited. Short-term variations are influenced by meteorological conditions, especially through temperature and moisture, via the microbial degradation of organic compounds, and the release of harmful substances (Kjeldsen et al., 2002; Mangimbulude et al., 2009). Precipitation can therefore induce either increased mobilisation of pollutants or a dilution effect (Kjeldsen et al., 2002; Tränkler et al., 2005). Leachate composition is also closely dependent on the type and quantity of waste (Øygard et al., 2011; Silva-Filho et al., 2006). Long-term variations depend strongly on climate, waste type and the degree of waste decomposition (Bozkurt et al., 2000; Kulikowska and Klimiuk, 2008). Leachate treatment before release into the environment is a necessity in many countries, because of significant concentrations of pollutants (Christensen et al., 2001), and because its toxicity must not endanger the quality of surface water and/or groundwater (Council Directive 1999/31/EC).

A simple and affordable way to treat landfill leachates is their collection and purification in lagooning systems by accumulation

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of the pollutants in the vegetation and at the bottom of the basins (Wojciechowska and Waara, 2011). During sedimentation, incorporation of trace metals into the solid phase is mainly controlled by three mechanisms: (i) precipitation of metal-bearing calcite, (ii) binding to Fe-oxyhydroxides and (iii) bonding to organic matter (Ettler et al., 2006a,b; Øygard et al., 2008). Another potential removal mechanism is by bioaccumulation in wetland macrophytes. This process is strongly influenced by seasonal variations in plant growth as well as by the concentration and mobility of trace metals in the surrounding water and sediment (Galletti et al., 2010; Grisey et al., 2012; Vymazal et al., 2007).

The landfill site of Etueffont (Territoire de Belfort, eastern France) is appropriate for investigating the purification processes taking place in lagooning systems. The present work provides a fine characterisation of sediments collected from upstream to downstream in the Etueffont lagooning system, based on physico-chemical parameters, mineralogy, and bulk sediment chemistry. The focus is on the behaviour of copper (Cu) and zinc (Zn) because they are often the most abundant trace metals in MSW landfills (Long et al., 2009), and are known for their relatively high mobility (Prechthai et al., 2008). Furthermore, when abnormally elevated quantities of these trace metals accumulate into the environment, they may produce toxic and irreversible effects on living organisms (Lejon et al., 2008; Maksymiec, 1997; Smith et al., 1999). The characterisation of lagoon sediments was completed with analyses of the leachates collected during two sampling campaigns at contrasted periods (wet and dry). The aim of our study was (i) to better understand the sedimentation dynamics of Cu

and Zn during the natural lagooning treatment of leachate and (ii) to evaluate the relative influence of the mechanisms controlling trace metal sedimentation in different sections of the lagooning system.

## 2. Materials and methods

### 2.1. Study area

This study was carried out from April 2009 to February 2010 in the MSW landfill of Etueffont in eastern France (Fig. 1; 47°43'18"N; 6°56'59"E). The site integrates a waste deposit area (28,000 m<sup>2</sup>) and a lagooning system (12,000 m<sup>2</sup>). It is located at a mean elevation of 475 m a.s.l., at the southern foot of the Vosges mountains on a bedrock of Devon-Dinantian shales, with a humid, continental climate, a mean annual temperature of 8 °C and mean annual precipitation of 1418 mm. The landfill was active from 1976 to 2002 and received household waste from 66 municipalities, corresponding to about 48,000 inhabitants. The construction of the present-day lagooning system began in 1994. The waste leachates are collected at the bottom of the waste layers and discarded into the lagooning system, which is composed of a settling pond and three lagoons (LA, LB and LC; Fig. 1). The settling pond is subdivided into three basins (B1, B2 and B3), separated by gravel filters with perforated drains in order to scavenge the particulate load. Detailed technical data of the Etueffont lagooning system are given in Table 1. The shore vegetation of the three lagoons consists mainly of cattails (*Typha latifolia* L.) and common reeds (*Phragmites australis* (Cav.)

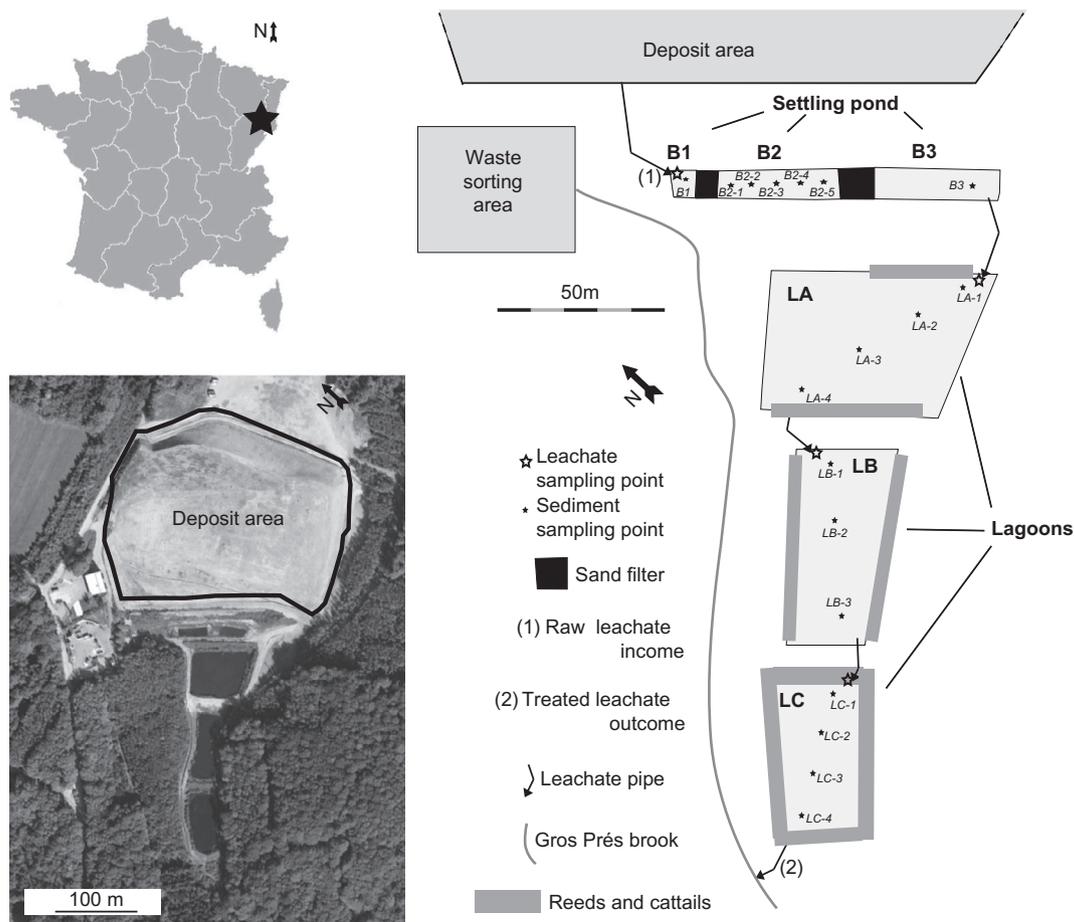


Fig. 1. Map of France, with location of Etueffont landfill (top left); aerial photo of the site (bottom left) and schematic map of the surface flow lagooning system with location of sampling points (right).

**Table 1**

Characteristics of the lagooning system of Etueffont. The position of each lagoon is shown in Fig. 1. Water depth remains constant over time, due to the presence of overflow discharge pipes.

Lagoon	Area (m <sup>2</sup> )	Water depth (m)	<sup>a</sup> Residence time of water (day)
B1 + B2 + B3	390	0.8	5
LA	1934	1.0	32
LB	1848	1.0	31
LC	1128	1.0	19

<sup>a</sup> Residence time is a theoretical value calculated considering the adjusted inflow was 59.4 m<sup>3</sup> day<sup>-1</sup> (Khattabi et al., 2002). Variations in flow rates result in modification of this retention time but relative differences between each lagoon remain unchanged.

Trin. ex Steud). Vegetation density increases downstream, with sparse vegetation in LA, becoming progressively invasive in LB and LC (Fig. 1). At the outlet of the lagooning system, the treated leachate is released into a local brook called “Gros Pré”.

## 2.2. Field sampling

In April 2009, an Ekman dredge was used to collect 18 sediment samples from upstream to downstream in the lagooning system. It was the first dredging campaign since the construction of basins; the samples thus contain the entire metal load accumulated since 1994. For each sampling point shown in Fig. 1 the complete sediment column was collected four times within an area of 1 m<sup>2</sup> and mixed to a composite bulk sample of 4–5 kg. A subsample of 1 kg (wet weight) was split from this bulk sample and stored in clean sample bottles. Afterwards, the sediments were dried in the laboratory at 40 °C and sieved at 2 mm mesh size. More than 90 wt.% of the dried samples had a grain size <2 mm.

The leachates were sampled in two campaigns: during a dry period with low leachate flow in May 2009, and during a wet period with high leachate flow in February 2010. Electrical conductivity (EC), redox potential (Eh), temperature and pH in the lagooning system were measured *in situ* with a WTW 340i portable apparatus at the inlet pipes of the settling pond and the three lagoons. Two litres of leachate were collected at each survey point (Fig. 1) with acid-cleaned bottles (HDPE), stored at 4 °C and analysed within two days after sampling.

## 2.3. Leachate analysis

The leachates were filtered with 0.45 µm cellulose acetate filters. The filtrate was analysed for total organic carbon by thermal oxidation (TOC 5000A, Shimadzu). Bicarbonates were determined by potentiometric titration; Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup> by high-pressure ion chromatography (Dionex DX 100); Ca by atomic absorption spectrometry (AA 100, Perkin–Elmer) and Fe, Cu and Zn by ICP-AES (Jobin Yvon 124). For the study of the particulate matter, the Total Suspended Solids (TSS) load was determined gravimetrically by weighing each 0.45 µm cellulose acetate filter before and after filtering, in both cases after drying at 40 °C. Half of the filter was then transferred into Teflon vials, ashed at 200 °C, completely dissolved in sub-boiled distilled 15 N HNO<sub>3</sub> and HF 40%, evaporated, and finally redissolved in 15 mL of 1 N HNO<sub>3</sub> for determination of Ca, Fe, Cu and Zn by ICP-AES. Blanks of filters were run simultaneously and revealed no contamination for any of the investigated elements.

## 2.4. General sediment analyses

The percentage of dry weight of the sediments was determined gravimetrically by weighing subsamples before and after drying in an oven at 105 °C. Bulk density was calculated after weighing a

known volume (100 cm<sup>3</sup>) of sediment. The procedure was repeated three times. pH was determined in a suspended solution (sediment/water ratio 1:5) in accordance with ISO 10390 (2005). Sediment colour was determined in the laboratory on dry and sieved samples using a Munsell Soil Colour Chart. The carbonate content was measured using the Bernard calcimeter method (ISO 10693, 1995). In order to quantify Fe bound to reducible oxides, extraction was performed using Tamm reagent (0.2 M) at 80 °C (Parat et al., 2003), and the Fe concentrations were then measured by atomic absorption spectrometry (AA 3300, Perkin–Elmer). X-ray diffractions (XRD) were performed on bulk sediment samples using Cu K $\alpha$  radiation scanning over the Bragg's angle (2 $\theta$ ) range of 2.5–60° with a step scan of 0.040° per 39.2 s (Bruker Endeavor D4).

## 2.5. Organic carbon and nitrogen content

Prior to analysis, one gram of sediment was decalcified at room temperature with 20 mL of 2 N HCl under continuous agitation for two hours and diluted with 120 mL of ultrapure water. After 12 h of decantation, supernatant was discarded and samples were rinsed by centrifugation with ultrapure water. Samples were then dried at 40 °C, finely crushed in an agate mortar and analysed in triplicate by dry combustion (Vario Cube CN mode, Elementar) to determine organic carbon content. A sulfanilamide standard was used (41.84% C and 16.27% N). The organic carbon content in bulk sediment was calculated as follows: Corg (%) = [1 – (CaCO<sub>3</sub> (%) / 100)] × Corg\* (%); with Corg (%): percentage of organic carbon in bulk sediment; CaCO<sub>3</sub> (%): percentage of CaCO<sub>3</sub> in bulk sediment and Corg\* (%): percentage of organic carbon in decalcified sediment. Total nitrogen concentrations were measured by dry combustion on bulk sediment samples using the same instrument.

## 2.6. Trace metal concentrations

Total Cu and Zn concentrations were determined by the following procedure: 0.2 g of sediment sample was mineralised in 10 mL Teflon vials at ambient temperature for 48 h in 5 mL of a mixture (1:1) of HNO<sub>3</sub> (65%) and HF (40%). Samples were then heated at 90 °C for 24 h, evaporated to dryness and dissolved in ultrapure water with 50 µL of HClO<sub>4</sub> (60%). Samples were evaporated again and dissolved in 20 mL of 1 N HNO<sub>3</sub>. The Cu and Zn contents were determined by atomic absorption spectrometry (AA 3300, Perkin–Elmer). Three replicates of each sample were mineralised and the Cu and Zn concentrations were measured three times on each replicate. The international certified reference materials IAEA soil 7 and GIT-IWG granite MA-N were analysed in each batch by following the same procedure in order to check the quality of the mineralisation procedure (Table 2).

## 2.7. Isotopic measurements

Measurements of  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  in CaCO<sub>3</sub> were performed on the particulate fraction after the filtration (0.45 µm cellulose acetate filter) of a one-litre sample of leachate collected at the inlet of the lagooning system. Before analysis, organic matter was

**Table 2**  
Certified and measured values (mean ± SD) of Cu and Zn concentrations in certified reference materials.

	Certified values	Measured values
<i>Cu</i> µg g <sup>-1</sup>		
IAEA Soil 7 (n = 5)	11	13 (±4)
GIT-IWG Granite MA-N (n = 3)	140	145 (±5)
<i>Zn</i> µg g <sup>-1</sup>		
IAEA Soil 7 (n = 5)	104	99 (±3)
GIT-IWG Granite MA-N (n = 3)	220	234 (±11)

removed with excess of H<sub>2</sub>O<sub>2</sub>. Isotopic analyses in the carbonate fraction (single measurement) were performed on a dual-inlet mass spectrometer (IsoPrime, Elementar). NBS19 certified reference material ( $\delta^{13}\text{C}_{\text{PDB}} = +1.95\text{‰}$ ;  $\delta^{18}\text{O}_{\text{PDB}} = -2.2\text{‰}$ ) and a marble internal standard ( $\delta^{13}\text{C}_{\text{PDB}} = -8.78\text{‰}$ ;  $\delta^{18}\text{O}_{\text{PDB}} = -17.23\text{‰}$ ) were used for normalisation. All results are expressed in delta notation where:  $\delta^{13}\text{C}$  (or  $\delta^{18}\text{O}$ ) =  $[(R_{\text{sample}}/R_{\text{std}}) - 1] \times 1000$ ;  $R_{\text{sample}}$  and  $R_{\text{std}}$  are the absolute  $^{13}\text{C}/^{12}\text{C}$  (or  $^{18}\text{O}/^{16}\text{O}$ ) ratios for sample and standard, respectively.  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values are reported in parts per thousand (‰) relative to the Vienna Pee Dee Belemnite (VPDB) standard.

## 2.8. Statistical analysis

In order to evaluate statistically significant differences of a given parameter between two groups of samples, a Mann–Whitney *U* test was used. The Pearson correlation coefficient was calculated to evaluate linear relationships between parameters. The software programs used for statistical analysis and curve fitting were Past 2.12 (Hammer et al., 2001) and Kaleidagraph 4.1 (Synergy Software, 2010).

## 3. Results

### 3.1. Leachate chemistry

The chemistry of the leachates (Tables 3 and 4) was significantly different for the sampling campaigns in April 2009 (dry conditions) and February 2010 (wet conditions). The pH values varied from 7.09 to 7.71, but showed no systematic evolution within the lagooning system. In contrast, Eh values increased from B1 to LC. All other parameters decreased from upstream to downstream for both campaigns. Higher concentrations of total suspended solids (TSS), TOC, Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup> were found for the wet winter period. For both periods, the TSS load decreased abruptly by more than 80% within the settling pond and decreased, for both campaigns, from the lagooning system inlet to the outlet of lagoon LC (Table 3). During the wet period, total Cu and Zn concentrations were respectively about 10 and 30 times higher than during the dry period. Calcium was almost entirely in <0.45 μm dissolved fraction, while Fe was far more abundant in the particulate phase and massively deposited in the basins of the settling pond (Table 4). The trace metals Cu and Zn were more evenly distributed between the particulate and the dissolved fractions.

### 3.2. General characteristics of lagoon sediment

The dry weights (DW) of the sediments were comprised between 19% and 52% (Table 5). In the settling pond, the values were

similar from B1 to B2-3, achieved a maximum of 44% for B2-4 and then decreased to 19% at the outlet of the third basin. In the lagoons, the DW values ranged from 19 to 52%, with higher values for the samples from the centre of the lagoons (samples LA-2, LA-3, LB-2, LC-2 and LC-3;  $37 \pm 7\%$ ) compared to the edge samples (samples LA-1, LA-4, LB-1, LB-3, LC-1 and LC-4;  $23 \pm 7\%$ ). The sediment changed in colour from dark brown in the settling pond to brown at the edges of the lagoons and pale brown in the centre. The bulk density of the sediments varied from 0.53 to 0.87 g cm<sup>-3</sup> with an average of  $0.7 \pm 0.1$  g cm<sup>-3</sup>. There was only slight variability of the bulk densities in the settling pond ( $0.67 \pm 0.08$  g cm<sup>-3</sup>). In the centre of the lagoons the values were higher ( $0.79 \pm 0.05$  g cm<sup>-3</sup>) than near the edges ( $0.68 \pm 0.11$  g cm<sup>-3</sup>). pH values ranged from 6.9 to 7.8, with lower values near the edges of LB and LC ( $7.2 \pm 0.2$ ) than in the centre ( $7.6 \pm 0.2$ ).

### 3.3. Characterisation of the mineral fraction

The highest carbonate concentrations of 337 mg g<sup>-1</sup> were found for sample B2-2 from the settling pond. Within the lagoons, the concentrations decreased and reached a minimum value of 21 mg g<sup>-1</sup> for sample LB-2 (Fig. 2a). Although not determined by XRD, Fe-oxyhydroxides were probably a major component in the sediment with Fe concentrations from 21.6 to 115.5 mg g<sup>-1</sup>. Within the settling pond, the Fe concentrations decreased abruptly, followed by a more continuous decrease from LA to LC (Fig. 2b). In the lagoons, Fe concentrations were slightly higher near the edges than in the centre. XRD analyses of the sediment from the entire lagooning system revealed the presence of the same mineral groups for all sediments (Fig. 3). The first group (clays, quartz, feldspars and micas) was probably of detrital origin, either from the bedrock or from waste particles, whereas the second group (including calcite, dolomite and gypsum) probably precipitated inside the landfill or within the lagooning system. Isotopic measurements performed on CaCO<sub>3</sub> in the particulate fraction showed that carbonates were enriched in <sup>13</sup>C ( $\delta^{13}\text{C} = 7.84\text{‰}$ ) and depleted in <sup>18</sup>O ( $\delta^{18}\text{O} = -5.59\text{‰}$ ).

### 3.4. Organic carbon and nitrogen content in lagoon sediment

Concentrations of organic carbon ranged from 18 mg g<sup>-1</sup> in LC-2 to 147 mg g<sup>-1</sup> in B1 with decreasing values from upstream to downstream (Fig. 4a). The decrease was most pronounced in the settling pond, with values from 147 mg g<sup>-1</sup> (B1) to 44 mg g<sup>-1</sup> (B2-5). In the lagoons, the data were more scattered, ranging from 18 mg g<sup>-1</sup> to 100 mg g<sup>-1</sup>. However, for each lagoon the values were significantly higher ( $p < 0.01$ ) near the edges ( $72 \pm 17$  mg g<sup>-1</sup>) than in the centre ( $31 \pm 27$  mg g<sup>-1</sup>). Nitrogen contents ranged from 1.4 mg g<sup>-1</sup> to 27.3 mg g<sup>-1</sup> and the spatial distribution was the same as for organic carbon ( $R = 0.957$ ).

**Table 3**  
Characteristics of the landfill leachate of Etueffont during dry and wet periods. Sampling campaigns were carried out in May 2009 and February 2010, respectively. EC = electrical conductivity; Eh = redox potential, corrected against the hydrogen electrode; TDS = Total Dissolved Solids; TOC = Total Organic Carbon; TSS = Total Suspended Solids; SI = Saturation Indices; n.m. = not measured.

Samples	T (°C)	pH	EC (μS cm <sup>-1</sup> )	Eh (mV)	TDS (mg L <sup>-1</sup> )	TOC (mg L <sup>-1</sup> )	TSS (mg L <sup>-1</sup> )	HCO <sub>3</sub> <sup>-</sup> (mg L <sup>-1</sup> )	Cl <sup>-</sup> (mg L <sup>-1</sup> )	NO <sub>3</sub> <sup>-</sup> (mg L <sup>-1</sup> )	SO <sub>4</sub> <sup>2-</sup> (mg L <sup>-1</sup> )	SI CaCO <sub>3</sub> (log unit)
<i>Spring dry period</i>												
B1	17.1	7.11	1830	n.m.	1423	30.6	18.2	852	101.4	6.2	100	0.77
LA	24.7	7.71	1189	n.m.	757	19.9	5.2	n.m.	46.9	2.5	274	-
LB	23.2	7.68	1085	n.m.	818	16.0	3.7	n.m.	35.9	8.8	270	-
LC	23.4	7.65	961	n.m.	625	13.7	2.6	n.m.	28.7	1.3	258	-
<i>Winter wet period</i>												
B1	7.8	7.20	2060	227	2207	85.2	48.7	718	39.0	22.4	857	0.54
LA	7.4	7.09	1640	247	1672	74.0	10.0	628	30.8	25.7	522	0.50
LB	3.8	7.38	1208	417	1056	64.3	4.8	438	27.4	19.6	277	0.62
LC	3.2	7.34	1076	438	870	55.9	4.3	381	25.1	17.5	209	0.28

**Table 4**

Concentrations of Ca, Fe, Cu and Zn in dissolved (<0.45  $\mu\text{m}$ ) and particulate (>0.45  $\mu\text{m}$ ) fractions of the landfill leachate of Etueffont (n.d.: not detected). Sampling campaigns during dry and wet periods were carried out in May 2009 and February 2010, respectively.

Samples	Dissolved fraction (<0.45 $\mu\text{m}$ )				Particulate fraction (>0.45 $\mu\text{m}$ )			
	Ca	Fe	Zn	Cu	Ca	Fe	Zn	Cu
	(mg L <sup>-1</sup> )				( $\mu\text{g L}^{-1}$ )			
<i>Spring dry period</i>								
B1	147	0.071	9.5	2.5	0.94	5.54	3.90	0.78
LA	95	0.062	8.9	2.0	0.35	0.36	1.56	0.25
LB	111	0.008	3.7	2.3	0.39	0.11	1.41	0.30
LC	90	0.007	7.3	2.1	0.24	0.28	1.78	0.42
<i>Winter wet period</i>								
B1	439	0.038	260	16	3.66	11.69	130.80	13.61
LA	313	0.039	70	6	0.58	2.17	12.94	2.37
LB	171	0.031	30	n.d.	0.24	1.00	3.59	0.72
LC	136	0.038	20	n.d.	0.11	0.77	n.d.	n.d.

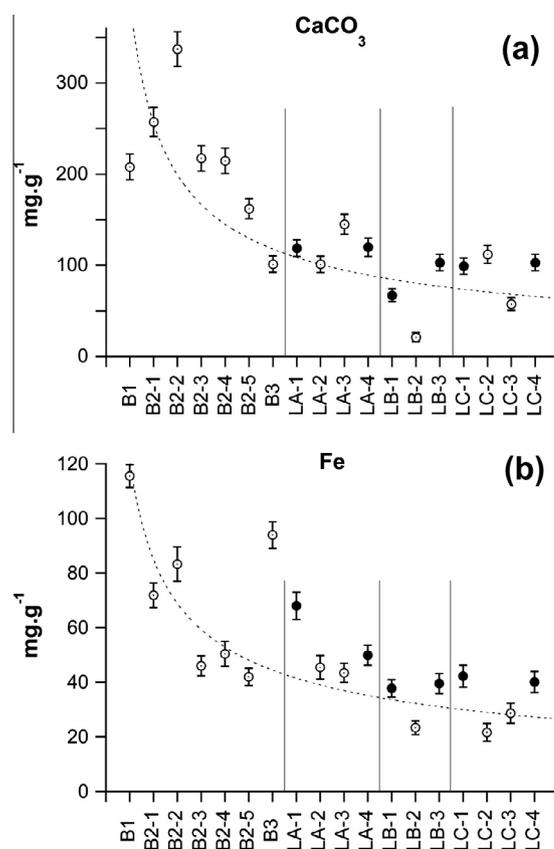
**Table 5**

Results of general sediment analyses. DW = dry weight.

	DW (%)	Munsell chart colour		Bulk density g cm <sup>-3</sup>	pH
B1	19	7.5YR 3/4	Dark brown	0.77	7.8
B2-1	21	10YR 4/2	Dark grayish brown	0.54	7.4
B2-2	21	10YR 4/2	Dark grayish brown	0.61	7.5
B2-3	27	10YR 4/2	Dark grayish brown	0.66	7.6
B2-4	44	10YR 4/3	Brown	0.72	7.6
B2-5	34	10YR 4/3	Brown	0.73	7.2
B3	19	10YR 4/3	Brown	0.71	7.1
LA-1	19	10YR 5/3	Brown	0.70	7.6
LA-2	32	10YR 6/3	Pale brown	0.76	7.7
LA-3	25	10YR 5/3	Brown	0.76	7.4
LA-4	19	10YR 5/3	Brown	0.75	7.4
LB-1	36	10YR 5/3	Brown	0.80	7.1
LB-2	52	10YR 6/3	Pale brown	0.87	7.4
LB-3	23	10YR 5/3	Brown	0.74	7.2
LC-1	20	10YR 4/3	Brown	0.55	6.9
LC-2	40	10YR 6/3	Pale brown	0.76	7.7
LC-3	38	10YR 6/3	Pale brown	0.79	7.5
LC-4	20	10YR 4/3	Brown	0.53	7.5

### 3.5. Trace metal concentrations in lagoon sediment

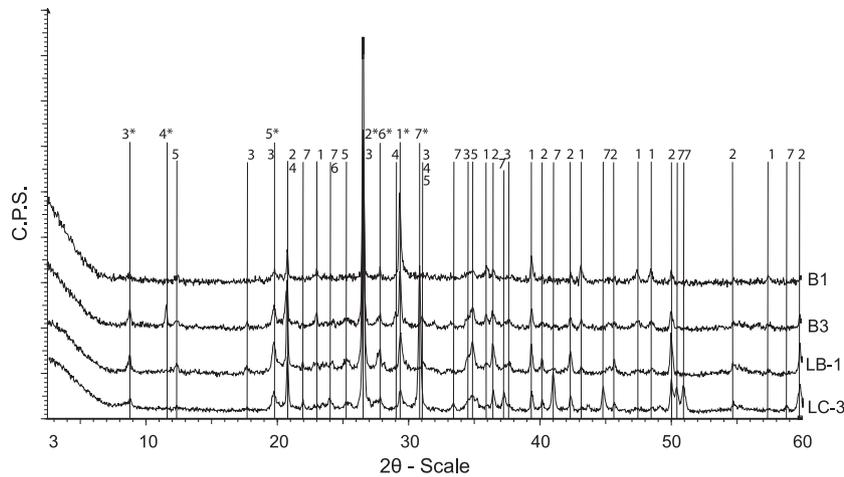
Different patterns were observed for Cu and Zn concentrations measured in sediment. The Zn concentrations are presented in Fig. 4b. A continuous decrease in Zn concentration was observed in the settling pond from B1 (1154  $\mu\text{g g}^{-1}$ ) to B3 (508  $\mu\text{g g}^{-1}$ ). In the lagoons, values ranged from 207  $\mu\text{g g}^{-1}$  to 963  $\mu\text{g g}^{-1}$ . The Zn concentrations in the sediment decreased from LA to LC with respective average concentrations of  $729 \pm 229 \mu\text{g g}^{-1}$  and  $379 \pm 198 \mu\text{g g}^{-1}$ . In each of the three lagoons, Zn concentrations in samples collected near the edges ( $697 \pm 184 \mu\text{g g}^{-1}$ ) were twice as high ( $p < 0.01$ ) as in samples from the centre of the lagoons ( $349 \pm 170 \mu\text{g g}^{-1}$ ). The Cu concentrations (Fig. 4c) measured in sediment from the settling pond were homogeneous, with an average value of  $130 \pm 26 \mu\text{g g}^{-1}$ . In the lagoons, Cu concentrations ranged from 101  $\mu\text{g g}^{-1}$  to 356  $\mu\text{g g}^{-1}$ , decreasing from LA to LC with respective average concentrations of  $276 \pm 66 \mu\text{g g}^{-1}$  and  $175 \pm 84 \mu\text{g g}^{-1}$ . As in the case of Zn, concentrations of Cu in samples from the edges ( $286 \pm 45 \mu\text{g g}^{-1}$ ) were twice as high ( $p < 0.01$ ) as in those from the centre of the lagoons ( $153 \pm 64 \mu\text{g g}^{-1}$ ).



**Fig. 2.** Concentrations of  $\text{CaCO}_3$  (a) and Fe (b) in the sediment of the Etueffont lagooning system collected in the settling pond and in the centre of the lagoons (open markers  $\odot$ ) and near the edges of the lagoons (filled markers  $\bullet$ ). For each sample, the error bar represents the highest value between the standard deviation of the three replicates and the experimental error. Vertical lines separate samples from the settling pond and the three lagoons.

## 4. Discussion

The pH and Eh values of the leachates of the Etueffont site fall into the typical range for a landfill in the methanogenic phase (Claret et al., 2011; Kjeldsen et al., 2002). This is in agreement with a previous study on the Etueffont landfill by Aleya et al. (2007), who reported that the site had already achieved advanced stable conditions in 2000, i.e. with pH reaching neutral values, methane production and a decreased release of organic and inorganic components, corresponding to the methanogenic phase.



**Fig. 3.** Diffractograms of four representative samples of lagoon sediment (B1, B3, LB-1, LC-3). Asterisks indicate the main diffraction peak of each identified mineral. Numbers are attributed to the different minerals. 1: calcite; 2: quartz; 3: micas; 4: gypsum; 5: clays; 6: feldspars; 7: dolomite.

In the settling pond, the sharp decrease in TSS demonstrates that particulate matter is efficiently scavenged by the sand filters. Within the lagooning system, the electrical conductivity, the total dissolved solid (TDS) contents and most of the elemental concentrations in the leachate decreased with flow distance (Tables 3 and 4), indicating that purification by sedimentation and other scavenging processes continues as the leachate flows downstream. However, all the information obtained on the purification processes taking place within the lagooning system must be considered qualitatively, since it was not possible here to quantify the effects of secondary modifications on leachate chemistry, through the dissolution of organic and inorganic particles, and/or dilution by rainwater (Johnson et al., 1999; Ettler et al., 2008).

Our leachate data thus show that leachate composition varied over time and that trace metal concentrations were subject to secondary modifications. Unlike leachates, sediments record the history of leachate purification since the construction of the wetlands. Fluctuations due to variations of leachate composition over time or secondary modifications are thus completely compensated. Our discussion on the behaviour of Cu and Zn within the lagooning system will therefore be mainly based on the sediment data.

The Cu and Zn concentrations measured in the Etueffont landfill leachate sediments were higher than reported in other studies (Ettler et al., 2006a; Silva-Filho et al., 2006; Wojciechowska et al., 2011) and in the higher range of those found by Øygaard et al. (2008).

The spatial distribution of Cu within the Etueffont landfill leachate sediments differed from the pattern observed for Zn, showing that their behaviour was different during migration and sedimentation.

Concentrations of Zn in the sediment decreased sharply in the settling pond where the highest Zn contents were measured in the first basin (Fig. 4b). We found that Zn was highly correlated with Fe and organic carbon in the sediment (Table 6) throughout the lagooning system. A significant correlation was also found between Zn and  $\text{CaCO}_3$ , but only for samples collected from the settling pond and from the centre of the lagoons (Table 6). With relatively stable concentrations in the settling pond, Cu did not show the same spatial distribution as Zn. The Cu concentrations remained low and stable in the settling pond and we found no correlations with other parameters. In contrast, in the lagoon sediments, Cu concentrations increased and the values were, as for Zn, highly correlated with organic carbon and Fe concentrations (Table 6).

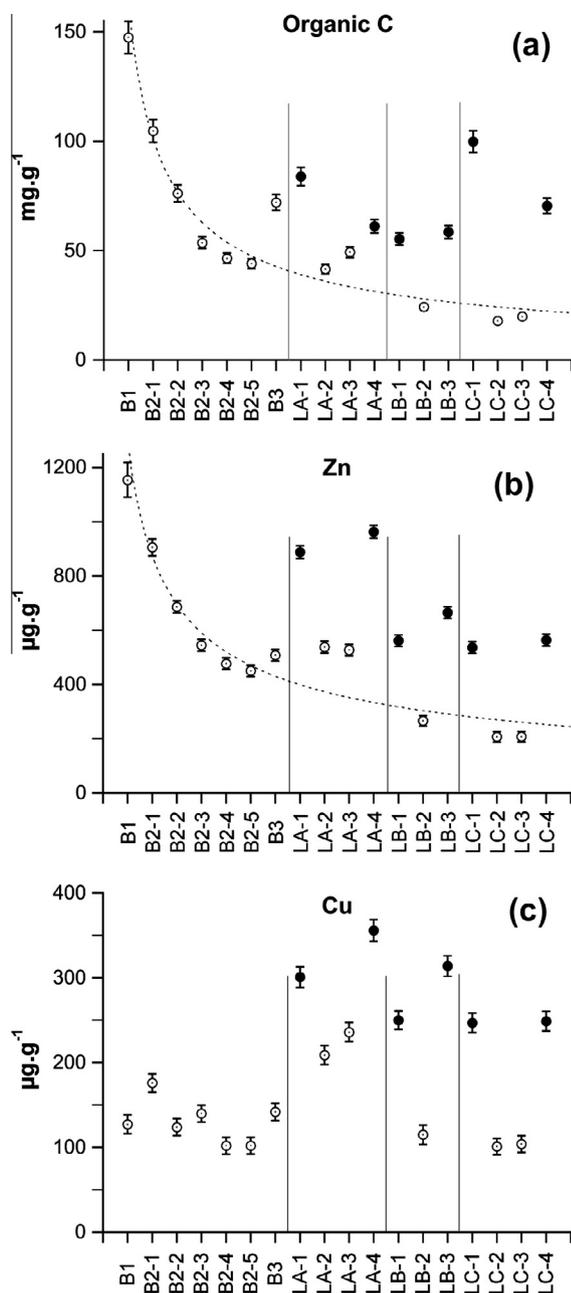
A similar contrasting behaviour for Cu and Zn has already been observed in earlier studies. E.g.; Li et al. (2009) found in a study on landfill leachates that Cu was more abundant than Zn in the colloidal fraction (comprised between  $0.45 \mu\text{m}$  and  $10 \text{kDa}^{-1}$ ), whereas Zn prevailed over Cu in the truly dissolved fraction ( $<1 \text{kDa}$ ). Similarly, Lyvén et al. (2003) and Dahlqvist et al. (2007) reported for natural waters that Cu was mostly combined with fine organic colloids, while Zn was rather present as a free ion or bound to larger Fe colloids. Øygaard et al. (2008) performed sequential extractions on landfill sediments and found that large portions of Zn and Cu were bound to Fe- and Mn-oxides. Furthermore, Zn was also fixed in carbonates, whereas significant portions of Cu were associated with the organic and residual fractions. Ettler et al. (2006a) likewise reported for landfill-affected stream sediments that Zn was mainly bound to Fe- and Mn-oxides and to a lesser extent to carbonates and organic matter. They also found a strong affinity of Cu for organic matter and the residual fraction.

These dissimilarities in mobilisation and in sedimentation processes can explain the contrasted behaviour observed for Cu and Zn at the landfill site of Etueffont.

The short residence time of the leachates in the settling pond (Table 1) indicates that the sedimentation of trace metals in this part of the lagooning system is mainly controlled by mechanisms with rapid kinetics, while processes that require more time are favoured in the lagoons.

The correlation between Zn and  $\text{CaCO}_3$  observed for the samples from the settling pond and the centre of the lagoons (Table 6) indicate that coprecipitation of Zn with carbonates occurred during leachate treatment. The highest  $\text{CaCO}_3$  concentrations were found in the settling pond (Fig. 2a), suggesting that calcite precipitation is highest during the first stage of leachate treatment. However, calcium and bicarbonate concentrations decreased in the subsequent lagoons (LA, LB and LC) synchronously with a slight rise in pH (Tables 3 and 4), showing that precipitation of newly formed calcite continues in the lagoons. The study of Ettler et al. (2006b) demonstrated through precipitation experiments that calcite precipitates spontaneously in such media, probably due to progressive degassing of  $\text{CO}_2$ . Manning (2001) investigated the morphology of calcite grains transported in landfill leachates and observed calcite

<sup>1</sup> kDa = kilo Dalton. 1 Dalton is equivalent to the unified atomic mass unit. 10 kDa correspond roughly to a diameter of 5 nm; but the exact relationship depends on the three-dimensional structure of the colloids (Dahlqvist et al., 2007).



**Fig. 4.** Concentrations of organic C (a), Zn (b) and Cu (c) in the sediment collected in the settling pond and in the centre of the lagoons (open markers ○) and near the edges of the lagoons (filled markers ●) in the Etueffont lagooning system. For each sample, the error bar represents the highest value between the standard deviation of the three replicates and the experimental error. Vertical lines separate samples from the settling pond and the three lagoons.

concretions and overgrowths on detrital quartz grains. Moreover, the  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  compositions of the particulate carbonate fraction of the Etueffont leachates are in agreement with the values reported by Manning (2001) and North et al. (2004) for newly formed calcite particles.

The additional correlations of Zn and Cu with Fe (Table 6) suggest that coprecipitation with Fe-oxyhydroxide particles is another process that could potentially remove Cu and Zn from the leachates. Higher Fe concentrations in the sediment were measured upstream and the values decreased with flow distance (Fig. 2b). In parallel, the redox potential was lower in the settling pond B1 and increased in the lagoons (Table 3), illustrating that the

leachates become progressively oxygenated within the lagooning system. There is therefore a link between progressive oxygenation of the leachate and precipitation of Fe-oxyhydroxides. The absence of crystalline forms of Fe in the sediment (Fig. 3) shows that iron precipitates as amorphous Fe-oxyhydroxides. Wojciechowska and Waara (2011) described a similar decrease in Fe concentrations for the leachates of a comparable lagooning treatment facility during the first purification step when the leachates were mixed with oxygenated surface water.

Organic matter is also involved in the purification process in lagooning systems. Organic C is typically found in the particulate and dissolved fractions of landfill leachates and is a major sediment component (Gonçalves et al., 2004). The strong correlations found for Cu and Zn with organic C in the Etueffont sediments (Table 6) demonstrate that organic C plays an important role in the sedimentation of these metals. The sequestration of organic carbon may result from: (i) the sedimentation of particulate organic matter, and (ii) the aggregation of dissolved organic matter (DOM), followed by sedimentation. The organic C content of the sediments (Fig. 4a) and the TSS data (Table 3) indicate that the first process occurs mainly in the settling pond. However, in the sediments of the settling pond, only Zn is correlated with organic C (Table 6). This shows, together with the relatively low Cu concentrations of sediments, that sedimentation of particulate organic matter in the settling pond scavenges Zn but almost no Cu. In contrast, in the lagoon sediments, both Cu and Zn are significantly correlated with organic C (Table 6), demonstrating that a second scavenging mechanism resulting in Cu and Zn sedimentation occurs in the lagoons. Most of the Cu and some of the Zn thus flow through the settling pond as dissolved ions and/or bound to organic colloids (Matura et al., 2010), followed by progressive sedimentation of both metals in the lagoons, together with organic C. This contrasting behaviour between settling pond and lagoons is probably mainly controlled by the residence times of the leachates, which are much longer in the lagoons than in the settling pond (Table 1). The progressive decrease in Zn and Cu concentrations measured in the dissolved fraction of the leachates for the winter period (Table 4) is in accordance with the hypothesis that flocculation and/or precipitation from the dissolved phase occurs, resulting in the sedimentation of trace metals.

Furthermore, our study reveals the influence of shore proximity on the sedimentation dynamics of Cu and Zn. For each lagoon, higher concentrations of these elements were systematically measured in the samples collected near the edges, which also contained higher concentrations of organic C. This pattern was never observed for  $\text{CaCO}_3$ , and only to a minor extent for Fe-oxyhydroxides. The decomposition of macrophytes from the bank area of the three lagoons is probably the main source of organic carbon, apart from the waste deposits themselves. Therefore it seems likely that organic matter from the shore vegetation controls the edge-effect dynamics observed for the sedimentation of Cu and Zn in the lagoons. The absorption of metals from the leachates by reeds and cattails was measured for LC during a complete study of this lagoon at the Etueffont site (Grisey et al., 2012). As macrophytes are not removed from the lagoons, their decomposition and the release of DOM along the lagoon edges may enhance the formation and sedimentation of Cu- and Zn-composed organometallic complexes. Moreover, the macrophytes roots provide an effective locally oxidizing environment leading to precipitation of Fe-oxyhydroxides on the root surfaces (Otte et al., 1995; Peverly et al., 1995). Because Cu and Zn have high binding affinity for Fe-oxyhydroxides, they may co-precipitate in iron plaques on the root surfaces. As slightly higher concentrations of Fe are measured near the edges, this mechanism is thought to occur in the lagoons but is considered to have a low impact on sedimentation dynamics. Finally, the density of stems, roots and rhizomes acts as a filter

**Table 6**  
Correlation matrices for sediment components for the whole lagooning system (top), the settling pond and the centre of the lagoons (middle up), the settling pond (middle down) and the lagoons separately (bottom).

	Fe	CaCO <sub>3</sub>	C	Cu	Zn	
Fe	–					<i>Whole lagooning system</i> (n = 18)
CaCO <sub>3</sub>	0.566*	–				
C	0.805***	0.447	–			
Cu	–0.083	–0.276	0.209	–		
Zn	0.725***	0.450	0.837***	0.463	–	
Fe	–					<i>Settling pond and centre of the lagoons</i> (n = 12)
CaCO <sub>3</sub>	0.546	–				
C	0.917***	0.592	–			
Cu	0.095	0.030	0.164	–		
Zn	0.851***	0.651*	0.974***	0.286	–	
Fe	–					<i>Settling pond</i> (n = 7)
CaCO <sub>3</sub>	0.009	–				
C	0.844*	0.174	–			
Cu	0.292	0.122	0.447	–		
Zn	0.727	0.329	0.976***	0.433	–	
Fe	–					<i>Lagoons</i> (n = 11)
CaCO <sub>3</sub>	0.569	–				
C	0.728*	0.419	–			
Cu	0.786**	0.550	0.752**	–		
Zn	0.880***	0.538	0.706*	0.958***	–	

\* p < 0.05.

\*\* p < 0.01.

\*\*\* p < 0.001.

for the leachate (Brix, 1994) and promotes the sedimentation of contaminants.

## 5. Summary and conclusions

This study underlines the effectiveness of lagooning systems for the purification of landfill leachates. Decreases in electrical conductivity, TSS and TDS contents and most of the elemental concentrations indicate the removal of pollutants from the leachates and their subsequent accumulation in the lagooning system sediments. Sediment analyses provide indications about the sedimentation mechanisms for Cu and Zn. A massive scavenging of Zn occurred in the settling pond, at the beginning of the treatment, where particles rich in Fe, calcite and organic C were trapped by gravel filters. In contrast, most of the Cu was not scavenged in the settling pond, but was exported to the lagoons probably as dissolved organic complexes or bound to organic colloids. Sedimentation processes in the lagoons are mainly controlled by the lower particulate load of the leachates, the longer retention time, increasing oxygenation and the input of fresh organic matter from shore vegetation. The presence of macrophytes results in a two-fold increase in Cu and Zn concentrations in the sediment, highlighting the preferential accumulation of pollutants near the lagoon edges. This preferential accumulation is thought to be controlled by inputs of organic matter due to macrophyte decomposition and to a lesser extent by a trapping of Cu and Zn by roots of shore vegetation. Our results thus confirm the interest of including vegetation in the design of lagooning systems receiving landfill leachate, in order to promote the retention of trace metals within the lagoons.

## Acknowledgements

This work was financed by a BQR PRES fund of the universities of Burgundy and Franche-Comté. The authors wish to thank the SICTOM (Solid Waste Management Service) of Etueffont for the authorisation to access the site. We also thank Carmela Chateau-Smith for her assistance with the English version, Pierre Pellenard, Jean François Deconinck, Nathalie Guichard and Ludovic Bruneau for XRD analyses and Bruno Régent for field sampling and leachate

analyses. The interpretation of the leachate data benefited from helpful discussions with Philippe Amiotte-Suchet.

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