# Study of trace metal-bearing phases in sediments from runoff water infiltration basins

Etude des phases porteuses des polluants métalliques dans des sédiments de bassins d'infiltration des eaux pluviales

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## ABSTRACT

The distribution of trace metals (Cd, Cr, Cu, Ni, Pb, Zn) in sediments of two infiltration basins in the area of Nantes (F) was determined using sequential and kinetic extractions associated with mineralogical analysis and SEM observations. The sequential extractions were conducted using the three-steps BCR protocol. The results showed quite similar distribution of trace metals in the two sediments, except for copper. Cadmium is mainly bound to the exchangeable fraction and Cr and Ni are mostly from the residual fraction. The major part of lead lies in the reducible fraction. zinc is concentrated in the exchangeable fractions and reducible. Cu is either mainly in the residual fraction for Boisbonne sediment, or equally distributed in exchangeable, oxidizable and reducible fractions. The comparison with the kinetic extractions let to associate the lability and non-extractability of trace metals to the fractions defined in sequential extractions. The observations by scanning electron microscope have confirmed the XRD analysis on the mineralogical composition of sediments and have highlighted the presence of bulky aggregates.

## **KEYWORDS**

Kinetic extractions, microscopic observations, sequential extractions, X-ray diffraction

# RÉSUMÉ

La distribution d'éléments trace métalliques (Cd, Cr, Cu, Ni, Pb, Zn) dans les phases solides de sédiments issus de deux bassins d'infiltration de la région nantaise a été étudiée au moyen d'extractions séquentielles et cinétiques associées à des analyses et des observations minéralogiques. Les extractions séquentielles, réalisées selon le schéma du BCR en trois étapes, montrent que la répartition des ETM est relativement comparable entre les deux sédiments, à l'exception du cuivre. Le cadmium est majoritairement lié à la fraction échangeable, le chrome et le nickel sont principalement issus de la fraction résiduelle, le plomb provient en majorité de la fraction réductible, le zinc est concentré dans les fractions échangeable et réductible et le cuivre est soit majoritairement résiduaire pour le bassin de Boisbonne, soit réparti équitablement entre les fractions échangeable, oxydable et réductible pour le bassin de Cheviré. La comparaison avec les extractions définies pour les extractions séquentielles. Les observations au microscope électronique à balayage ont confirmé les analyses DRX quant à la composition minéralogique des sédiments et ont mis en évidence la présence d'importants agrégats.

## MOTS CLÉS

Diffraction des rayons X, extractions cinétiques, extractions séquentielles, observations microscopiques

## 1 INTRODUCTION

It is now widely recognised that urban and road runoff waters carry significant loads of pollutants, including heavy metals, hydrocarbons, pesticides, bacteria and nutrients (Chebbo, 1992; Legret et al. 1997; Pagotto, 1999; Sansalone et al. 1997). They are likely to be harmful to the environment and may also be a threat to human health by migrating towards ground water or by accumulating in plants. These pollutants are partly accumulated in sediments of river and infiltration basins.

The mobility and bioavailability of trace metals are the result of their reactivity in sediments, in other words, their localization in different sediment components which is now usually called speciation. Characterizing trace metals in sediments has to go beyond a simple determination of total content. Speciation is necessary and may be performed using physical or chemical methods (Cornu et Clozel 2000). The physical methods are generally not sufficiently sensitive, and therefore can only be used for this purpose with highly contaminated samples. Chemical methods are more sensitive, and consist of using different reagents for extraction of metals.

Despite criticisms (Etcheber et al., 1983), sequential extractions are the most frequently used method for trace metal localization in sediments, the most widely applied being those proposed by Tessier et al. (1979). A large number of procedures have been developed (Flores-Rodriguez et al., 1994; Gomez Ariza et al., 2000; Van Herreweghe et al., 2003; Ciceri, 2008; Jamali et al., 2009) which differ from each other by the reagents and operating conditions used. The European Community Bureau of Reference (BCR) has proposed an optimized three-step procedure, including an application for sediment with the production of Certified Reference Material (Quevauviller et al., 1993; Rauret et al., 1999). According to this procedure, the first extractible fraction is the exchangeable related to clay, carbonates and amorphous phases, the second is the reducible related to metal oxides and the third is the oxidisable related to the organic matter.

Kinetic extractions are also a widely used method to determine the speciation of trace metal in soils or sediments, particularly considering kinetic aspects that also characterize the stability of the various trace metal–sediment constituent association (Bermond et al., 1998). For a given chemical agent, the kinetic extraction approach generates two kinds of data: (i) the proportion of metal extracted with respect to the total metal content of sediment sample; (ii) the kinetic behavior of metals. It has been suggested that such kinetic extraction can be modeled by two different pools (Labanowski et al., 2008). Although chemical extracted metals, called "labile" by Fangueiro et al. (2005), and the second pool of more slowly extracted metals, called "non labile", might be reasonably attributed to potentially "mobile" and/or "bioavailable" metal pool (Bermond et al., 2005). Several reagents are used for the extractions but the Ethylene diamine tetraacid (EDTA) is a well known strong chelating agent and has been widely used in soil study for estimating the total extractable metal pool. As EDTA is a non specific reagent, it was reported to remove metals organically bound as well as in oxides or secondary clay minerals (Payà-Pérez et al., 1993; Irene et al. 1999).

The objective of the present article was to study the trace metal-bearing phases of two sediments from runoff infiltration basins. The methodology used is based on the comparison of sequential and kinetic extractions in order to define the distribution of trace metals on the different solid phases of the material (Cornu et al. 2004). To support the results of extractions, mineralogical analysis and Scanning Electron Microscope observations were performed to assess the nature of mineral phases of the sediment (Cappuyns et al., 2007).

## 2 MATERIAL & METHODS

#### 2.1 Sites description and sampling

Two stormwater infiltration basins located in Nantes (west of France) were sampled. The first one, named Cheviré basin, is located in the south west of Nantes, it receives runoff waters from a 19,000 m<sup>2</sup> contribution area of the south part of the Cheviré bridge which is a section of the Nantes ring-road. Opened in 1991, the Cheviré bridge now carries an average daily flow of 90 000 vehicles. The second basin, named Boisbonne, is located in the East of Nantes, the drained runoff waters come from a 16,000 m<sup>2</sup> contribution area of the A11 highway. The average daily flow is about 27 000 vehicles per day. The Boisbonne basin is in use since the opening of the A11 in 1992 and had never been dredged since this date.

Basins have spatial heterogeneities which induce an uneven distribution of water. Thus, in order to have a global vision of the two basins, sediments sampling was conducted on 3 zones for Boisbonne

(Figure 1-a) and 4 zones for Cheviré (Figure 1-b) according to the frequency and speed of flooding in the area. A representative sample was composed of a homogeneous mixture of 6 to 13 shots with a distribution grid system for each area. Sampling was carried out following the recommendations of the technical guide "Recommandations pratiques pour la gestion des produits de l'assainissement pluvial" (C. Hébrard-Labit, 2006).



Figure 1: Sampling zones in the Boisbonne (a) and Cheviré (b) basins

#### 2.2 Physico-chemical and mineralogical sample characterization

Total element content, especially trace metal concentration (Cd, Cr, Cu, Ni, Pb and Zn) were determined on samples sieved to 2 mm and dried at 40 ° C. The term "total" is used here as the amount of metal dissolved according to the acid attack (NF X 31-147), the dissolution was performed with HF and HClO<sub>4</sub> acids. The quality of the analytical data for the acid attack was assessed by carrying out analyses of the certified reference material BCR-320 (river sediment).

The analysis was performed using ICP-OES (Inductively Coupled Plasma – Optical Emission Spectrometer) (Varian 720-ES). The quantification limit for Cd, Cr, Cu, Ni, Pb and Zn are respectively 0.5, 5, 2, 10, 10 and 2µg/L. In case of concentration under the limit of quantification, the sample was analyzed using ICP-MS (Inductively Coupled Plasma – Mass Spectrometer) (Varian 820-MS). The ICP-MS limit of quantification for trace elements is ranging from 0.02 µg/L to 0.3 µg/L depending on the element.

The SEM (Scanning Electron Microscopy) used for this study is an Hitachi S 570 with LaB6 tip excited by a source that can produce up to 30kV. In addition to the picture, a qualitative analysis of the basic structure is made using an EDX (Energy Dispersive X-ray spectroscopy) probe which can save energies of 1000 to 10 000 eV.

Major crystalline phase identification was by X-ray Diffraction (XRD) on powered samples with Brüker "D8 Advance" powder diffractometer operated in Bragg-Brentano geometry. The phase identification was performed using EVA software in conjunction with the Powder Diffraction File (PDF) database.

#### 2.3 Sequential extraction

The BCR sequential extraction protocol was applied to assess trace element fractionation in the samples. The extraction procedure was conducted on 2g dry sample (uncrushed and sieved to 2 mm): Step 1: extraction with 80 mL of acetic acid (0.11 M, stirred 16h); Step 2: extraction with 80 mL hydroxylamine hydrochloride (0.1 M, pH 2, stirred 16h); Step 3: extraction with 20 ml of H<sub>2</sub>O<sub>2</sub> 8.8 M (2 x 1h, 85°C) followed by an extraction with 100 mL ammonium acetate 1M (pH 2, stirred 16h). A fourth step (Step 4) was added consisting of mineralization of the final residue by use of a mixture of concentrated HF/HClO<sub>4</sub>. The liquid-solid separation is performed by centrifugation and filtration of the supernatant at 0.45 $\mu$ m Whatman (n°40) filter. The quality of the analyses was assessed by analyzing a reference sediment BCR-527 (lake sediment), using the same procedures. Blank tests were also introduced in each series. Cd, Cr, Cu, Ni, and Pb concentrations are under the quantification limit of the ICP-AES and ICP-MS. Zn concentration is less than 0.01 mg/L which is negligible by comparison to Zn concentration in liquid the samples (over 10 mg/L).

The sequential extraction procedure was carried out on four samples for each zone of the two basins, Boisbonne (BB1 to BB3) and Cheviré (CH1 to CH4), reference material and blanks of the different

extractants were added. After each extraction step, one sample of each series was dried at 40°C and put aside for XRD-analysis and SEM-observations (except the reference material). The analysis of metals was performed using an ICP-OES and/or ICP-MS as described above.

#### 2.4 Kinetic extraction

The EDTA kinetic extraction was conducted on a 1g dry sample of basin sediments. The sample and 50 mL of pH 7 solution of EDTA (0.1 M) were stirred using a rotary stirrer for 12 mixing times ranging from 5 min to 72 h. The liquid-solid separation is performed by centrifugation and filtration of the supernatant at 0.45  $\mu$ m Whatman (n°40) filter. Blank tests were added for each mixing time. The analysis of metals was performed using an ICP-OES and/or ICP-MS as described above. As for sequential extractions the blanks concentrations for trace metals are negligible.

The curves of kinetic extraction are modelled using a double exponential function (Labanowski et al., 2008). Three compartments associated with two reaction rates were defined: (i) a labile compartment  $Q_L$ , associated to a kinetic constant  $k_L$ , (ii) a non-labile compartment  $Q_{NL}$ , associated to a kinetic constant  $k_{NL}$  and (iii) a non-extractable compartment  $Q_{NE}$ .

#### 3 RESULTS AND DISCUSSION

#### 3.1 Sequential extraction

The mass balance was calculated by dividing the sum of concentrations of an element in the four extractions steps by the total concentration (Tables 1 and 2).

The balances were in the range 71 to 96%. In 70% of the case, the recovery is over 80%. The poor recovery can be explained by the washing with water between two extraction steps. It can also be explained by losses in step three when  $H_2O_2$  is added, indeed spattering has been observed.

The concentrations of Cd, Cr, Cu Ni, Pb and Zn of BCR-527 in the three BCR procedure steps are in good agreement with the certificated values with a difference ranging from  $\pm 1$  to  $\pm 20\%$ . The highest difference is observed for step 3, for the same previously explained reasons.

Metal contents in the various operationally-defined fractions, total concentrations and their mass balances are given in Table 1 for the Boisbonne samples and in Table 2 for the Cheviré samples.

In term of total concentrations, Cheviré samples present higher concentrations than Boisbonne samples for all the trace metals. The metals found in highest concentration are lead (33 to 368 mg.kg<sup>-1</sup>), copper (27 to 365 mg.kg<sup>-1</sup>) and zinc (131 to 1863 mg.kg<sup>-1</sup>).

The speciation of cadmium is characterized by a strong mobilization within the exchangeable fraction whatever zone or basin (45 to 66%). For BB1, BB2, BB3, CH3 and CH4 reducible phases (step 2) contain a higher percent of Cd (20 to 39%) than the oxidisable (step 3) fractions (2 to 11%). For CH1 and CH2, the percentage of Cd is similar ranging from14 to 19%. The residual phase is almost nonexistent (step 4).

For chromium the results of distribution are homogeneous. Cr is principally concentrated in the residual fractions (52 to 75%), in the oxidisable fractions (7 to 19%) and in lesser proportion in the reducible fractions (0.8 to 6%) and exchangeable fractions (0.2 to 3%).

The copper trend in the different samples is heterogeneous. In the Boisbonne basin samples the residual (29 to 51%) and oxidisable (13 to 26%) fractions contain the higher rates of Cu. In the Cheviré basin samples the exchangeable (22 to 32%) and oxidisable (20 to 28%) fractions contain the higher rates of Cu.

Nickel is mainly in the residual fraction (19 to 51%) as well as in the exchangeable fraction (16 to 38%), except for CH2, CH3 and CH4 (respectively 13, 10 and 7%) in which this fraction has the least contribution. For all the samples, reducible and oxidisable fractions have an equal contribution.

Lead is mainly contained in the residual fractions (33 to 38%) for Boisbonne basin samples and in the reducible fraction (34 to 40%) for the Cheviré basin. Oxidisable fraction has an intermediate contribution (12 to 27%), whereas the exchangeable fraction is only 1.6 to 7%.

Table 1 – Metal contents (in %) in the various operationally-defined fractions, total concentrations and mass balances for Boisbonne basin zones

Metal / Sample	Exchangeable (% of total)	Reducible (% of total)	Oxidisable (% of total)	Residual (% of total)	Total concentration (mg.kg <sup>-1</sup> )	Balance (%)
Cadmium						
BB1	<mark>53</mark>	<mark>39</mark>	4	<0,05	1,23	96
BB2	<mark>66</mark>	20	2	<0,05	0,38	88
BB3	<mark>45</mark>	<mark>31</mark>	7	<0,05	0,37	83
Chromium						
BB1	0,2	2	8	<mark>62</mark>	54,2	71
BB2	0,2	1	7	<mark>75</mark>	43,2	83
BB3	0,2	1	7	<mark>62</mark>	53,6	70
Copper						
BB1	7	8	26	29	58,9	71
BB2	12	11	13	<mark>51</mark>	27,2	87
BB3	5	5	20	<mark>42</mark>	30,1	71
Nickel						
BB1	<mark>38</mark>	22	9	19	74,5	88
BB2	<mark>34</mark>	10	6	<mark>41</mark>	33,5	91
BB3	28	14	8	29	38,7	79
Lead						
BB1	1	20	19	<mark>33</mark>	41,4	74
BB2	3	27	12	<mark>38</mark>	32,1	80
BB3	2	23	18	<mark>33</mark>	31,3	76
Zinc						
BB1	<mark>51</mark>	22	6	14	479,9	93
BB2	<mark>36</mark>	11	6	<mark>36</mark>	131,5	88
BB3	<mark>30</mark>	12	7	<mark>29</mark>	139,1	78

Table 2 – Metal contents (in %) in the various operationally-defined fractions, total concentrations and mass balances for Cheviré basin zones

Metal / Sample	Exchangeable	Reducible	Oxidisable	Residual	Total concentration	Balance
	(% of total)	(% of total)	(% of total)	(% of total)	(mg.kg <sup>-1</sup> )	(%)
Cadmium						
CH1	55	15	14	<0,05	0,47	84
CH2	56	19	16	<0,05	0,84	91
CH3	<mark>49</mark>	22	11	<0,05	0,93	91
CH4	<mark>55</mark>	26	10	<0,05	1,18	82
Chromium						
CH1	3	6	16	<mark>65</mark>	48,3	90
CH2	1,2	6	18	<mark>58</mark>	74,1	84
CH3	0,6	5	19	<mark>53</mark>	79,1	75
CH4	0,6	6	17	<mark>52</mark>	92,0	78
Copper						
CH1	<mark>32</mark>	24	20	9	190,4	85
CH2	<mark>32</mark>	22	25	9	334,8	88
CH3	22	18	28	11	320,2	81
CH4	26	21	24	10	365,7	78
Nickel						
CH1	16	12	10	<mark>51</mark>	20,0	89
CH2	13	13	13	<mark>46</mark>	29,6	85
CH3	7	12	14	<mark>47</mark>	32,5	79
CH4	10	13	12	<mark>43</mark>	37.4	79
Lead						
CH1	5	<mark>40</mark>	21	24	70,1	90
CH2	7	<mark>38</mark>	22	17	151,6	84
CH3	4	<mark>34</mark>	27	15	250,4	84
CH4	3	37	27	17	368,1	80
Zinc						
CH1	<mark>55</mark>	25	7	6	783,7	93
CH2	50	<mark>29</mark>	10	7	1273,9	96
CH3	27	<mark>32</mark>	13	9	1713,8	82
CH4	36	<mark>30</mark>	9	7	1863,5	81

Zinc is mostly contained in the exchangeable fractions (27 to 55%), the reducible fraction ranges from 22% (BB1 sample) to 32% (Cheviré basin). In BB2 and BB3 samples the Zn amount of the residual fraction is fairly high (36 and 29% respectively). The oxidisable fraction has the least contribution (6 to 13%).

The sequential extraction results on Cheviré basin are consistent with Clozel et al., (2006) and Durand (2003), except for lead for which they observed a strong mobilization within the oxidisable fraction.

#### 3.2 Kinetic extraction

Metal contents in the three compartments  $(Q_L, Q_{NL}, Q_{NE})$  and their total concentrations are summarized in Table 3 for all the samples.

The experimental difficulties were encountered for cadmium (mass balance often> 100%). In the 3 satisfying experiences in terms of mass balance, Cd is mainly extractible (( $Q_L + Q_{NL}$ ) between 62 and 76%), in BB2 and CH1 50% of Cd is in the labile fraction. For BB3, the distribution is equal between the 3 fractions.

Table 3 – Trace metals contents (%) in  $Q_L$ ,  $Q_{NL}$ ,  $Q_{NE}$  (labile, non labile, non extractible) compartments and the total concentrations (mg.kg<sup>-1</sup>) for the two basins

Metal/Sample	Q	Q <sub>NI</sub>	Q <sub>NE</sub>	Total concentration
	% of total	% of total	% of total	(mg.kg <sup>-1</sup> )
Cadmium				
BB1	*	*	*	1 23
BB2	50	23	27	0.38
BB3	28	34	38	0.37
	10	27	24	0,37
	*	*	*	0,47
	*	*	*	0,04
				0,93
CH4				1,18
Chromium				
BB1	1,3	3	<mark>96</mark>	54,2
BB2	1,1	3	<mark>96</mark>	43,2
BB3	1,1	2	<mark>97</mark>	53,6
CH1	3	9	<mark>88</mark>	48,3
CH2	2	7	<mark>91</mark>	74,1
CH3	2	7	<del>91</del>	79,1
CH4	2	6	92	92,0
Copper				- ,-
BB1	77	29	<0	58.9
001	01	18	<0	27.2
DD2 DD2	51	16	22	27,2
	57	70	33	30,1
CHI	00	31	9	190,4
CH2	67	<mark>43</mark>	<0	334,8
CH3	74	23	2	320,2
CH4	97	20	<0	365,7
Nickel				
BB1	<mark>71</mark>	<mark>29</mark>	<0	74,5
BB2	<mark>42</mark>	0,5	<mark>57</mark>	33,5
BB3	<mark>48</mark>	0,2	52	38,7
CH1	9	14	77	20.0
CH2	14	12	74	29.6
CH3	11	12	77	32.5
CH4	7	12	81	37.4
Load	1	12	07	01,4
	60	26	4	41.4
	03	30	1	41,4
BB2	50	<mark>34</mark>	10	32,1
BB3	45	22	33	31,3
CH1	<mark>56</mark>	34	10	70,1
CH2	<u>60</u>	38	3	151,6
CH3	*	*	*	250,4
CH4	<mark>64</mark>	<mark>33</mark>	2	368,1
Zinc				
BB1	*	*	*	479,9
BB2	70	17	13	131.5
BB3	43	18	38	139.1
CH1	43	32	25	783 7
CH2	34	32	22	1273 0
CU2	22	17	61	1712 0
	22	17	57	17 13,0
CH4	27	21	52	1863,5

\* Mass balance over 100%

Chromium is non extractible to more than 88% for Cheviré basin samples and more than 96% for the Boisbonne basin samples.

Copper is mainly labile (51 to 97%) and fairly non labile (16 to 43%). Except for BB3, Cu is almost nonexistent in the non extractible compartment.

For BB1 sample, nickel is very labile (71%), for BB2 and BB3 samples Ni is half labile and half non extractible. For Cheviré basin samples, nickel is almost (74 to 81%) non extractible.

Except for BB3, lead is extractible. For BB1, CH2 and CH4 samples, lead is very labile respectively 63, 60 and 64%.

For BB1, BB2 and BB3 samples zinc is respectively very (75 and 70%) and fairly labile (45%). For CH1 and CH2 samples, one third Zn is labile, one third non labile and one third non extractible. CH3 samples Zn is half labile and half non extractible and for the CH4, Zn is mainly non extractible (61%).

The distribution of trace metals between the three compartments could be summarized as follows: the labile compartment have a high content of Cd, Cu and Pb; the non labile compartment content are ranging from 2 to 40% depending on the trace metal and the non extractible fraction present a high amount of Cr, Ni and Zn;.

The comparison with results from the literature is not relevant because kinetic extractions were only performed on contaminated soils.

#### 3.3 Kinetic and sequential extraction comparison

Kinetic and sequential extractions can be used to compare the speciation of trace metals and mobility potential. Therefore, it is interesting to confront the proportion relative to the total concentration of each fraction of the sequential extraction and each compartment of the kinetic extraction. While not exactly proportional, the comparison of the rates of the four fractions and three compartments allows to draw some trends.

Cadmium in the exchangeable fraction appears to be labile, Cd in reducible and oxidisable fraction is non labile and Cd in the residual fraction is non extractible.

The behavior of chromium is coherent for all samples, Cr of residual and oxidisable fractions is clearly non extractible.

For the copper no clear trend between sequential extraction fraction and kinetic extraction compartments can be deduced.

The lead from the reducible fractions for Cheviré samples and from both the reducible and the residual fractions for Boisbonne samples seems to be labile. The non extractable fraction corresponds to the exchangeable fraction. By deduction Pb from the oxidisable fraction can be considered as non labile.

For nickel and zinc, the labile compartment corresponds to the exchangeable fraction and the non extractible from the residual fractions. The fraction of non labile nickel could be related to the reducible or to the oxidisable fraction.

It can be drawn that the trace metals from the oxidisable or organic matter fraction seems to correspond to the non labile or the non extractible compartments, while the exchangeable fraction corresponds (except for the lead) to the labile compartment.

In terms of strength of bounding between trace metals and solid surfaces, pollutants are strongly adsorbed on organic phases (oxidisable fraction) or included tightly in the residual fraction as revealed by the level of extraction from the non labile or the non extractible compartment. As described in the literature, trace metals (except for the Pb) on exchangeable fraction can be easily desorbed by EDTA and are quantified in the labile compartment. Nothing can be deduced for the reducible fraction from these experiments.

#### 3.4 Mineralogical analysis and SEM observations

#### 3.4.1 XRD and phase identification

The primary minerals found in the Boisbonne and Cheviré sediments according to XRD analysis (Figure 2) are quartz, muscovite (mica), albite (feldspar), microcline (feldspar) and clinochlore (chlorite). Figure 2 shows the diffractogram of zone 3 from Cheviré basin (CH3), which is representative of the general appearance of the diffractogram for the different zones of the two basins.

A disappearance of the 14.3 Å peak at step 3 can be noted, reflecting the dissolution of chlorite phase (Ryan et al., 2002).



Figure 2 : XRD analysis on a Cheviré sample (zone 3) for the different sequential extraction steps

#### 3.4.2 SEM observations and EDX analysis

A first series of samples was observed by SEM. The untreated sample, the first three steps of sequential extraction residues and the residue after 72h of contact with EDTA for sample CH4 have been compared.

Whatever the sample, no trace metal was analysed with EDX. Minerals such as quartz, feldspar, mica and clay have been observed which is consistent with XRD analysis. The presence of aggregates composed of the minerals and a binding phase which we believe to be organic matter has to be noticed. Such aggregates were previously mentioned by Badin (2009) in sediment from Lyon (France) infiltration pond.



Figure 3: SEM picture of the untreated CH4 sample (x 500) showing the different phases

After the first and the second steps of the sequential extraction, minerals appear to be more damaged. The reason could be the effect of reagent or the frictional effects during stirring. The aggregates have the same aspect as before the extraction.

After the third step, the aggregates are partly destroyed or broken, this explains that the particles sizes seem to be finer. This observation is consistent with the work of Badin (2009), which shows that  $H_2O_2$ , damages the aggregates with a resulting size decrease.

After 72h of contact with EDTA, the observations are almost the same as the untreated, with a slight damage on the minerals.

In view of this observation, the damage of the mineral is mainly due to the reagent effects. Furthermore, at this stage, it's hard to evaluate the relative contribution of organic matter and clays as binder.

#### CONCLUSION

Results of kinetic and sequential extractions performed on two sediments from infiltration basins were compared for Cd, Cr, Cu, Ni, Pb and Zn, supporting by XRD analysis and SEM observations.

The comparison shows that Cd from exchangeable fraction is labile and that Cr and Ni contained in the residual fraction are not extractable. Zn in exchangeable and reducible fractions and Pb bound with the reducible fraction are labile. No clear trend can be drawn for Cu, however Cu is very labile.

The results of this study show that each trace metal has its own behaviour towards the different fractions and in the different samples. Otherwise, it raises the question of the trace metal sources which may explain the different behaviors. It is, therefore, difficult at this stage to draw general conclusions on metal behaviour.

Only one method is not sufficient to explain the speciation and the mobility of the trace metals in the different fractions and this study highlighted the complementarity of the two extractions for a better understanding of the trace metal distribution among solid phases. This simple to implement methodology could serve as tools for rapid assessment of trace metals behaviour for the management of sediment from storm water infiltration basins for their treatment or reuse.

To go further, a methodology to separate the solid particles contained in aggregates should be developed to observe the trace metal-bearing phases and not only operational fractions.

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