

Characterisation and modelling of the interactions between pollutants and solid matrix in mixed contaminated urban soils

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Abstract

Facing public health priorities, authorities are concerned with environmental issues, such as water resource protection and soil preservation. In urban areas, former craft and industrial areas and water management practices are potential sources of diffuse pollution. Technicians to evaluate the impact of pollution usually use risk assessment tools, but developments are needed to take into account the physical and biochemical complexity of urban soils. This work carried out within the framework of a multidisciplinary research project is aimed at understanding the influence of mixed contamination on the adsorption/release phenomena of pollutants. Samples from two experimental sites will be analyzed for trace metals and organic substances. Analytical procedures should be developed to extract the pollutant-bearing phases before identification. Then experiments will be performed to study the speciation of pollutants as they are released and propose a model of soil-pollutant interactions.

Keywords

Urban water, contaminants, risk assessment, organic and inorganic pollutants, characterisation, modelling

INTRODUCTION

To control build-up area's extension and to fulfil people wishes in terms of life's quality improvement, soil preservation became a national and European priority. For the local authorities, the aim is to limit primeval sites and manage the potentially contaminated area.

In urban and suburban environments, the degradation of soils and water resources may result from craft or industrial activities, the re-use of industrial by-products in civil engineering, water management practices ... The authorities are highly concerned with the impact of soil pollutions on human health, and waiting forward management solutions for contaminated areas. Currently, the available tools used in urban management project are not taken into account the specificities of urban soils in terms of structural and biogeochemical complexity. Improvements of these tools require a multidisciplinary approach.

This study is developed in the framework of a research project (POLESUR) on soil and water pollutions in urban areas.

The aim of this study is to address part of this complexity through characterisation of the mixed pollution within specific urban soils, and through the modelling of the interactions between pollutants (trace metals and organic compounds) and solid matrix.

The review of the literature of urban soils indicates that most of the studies focus on the characterisation and treatment of industrial soils and stormwater drainage. The most frequently studied sites are heavily contaminated industrial sites and retention/infiltration ponds.

Those studies describe retention process of the pollutants in the soil as the ions exchanges, the surface complexation, the precipitation or the hydrophobic interactions “WEBER et al. (1991)”. Studies also define the factors influencing the retention of the pollutants “DURIN et al. (2005)”, such as pH, oxido-reduction conditions or ionic force. “CLOZEL et al. (2005)” describe the trace metals mobility and put forward the solid phases which bear the pollutants. The originality in this study lies in the consideration of the mixed pollution in soil and in the qualitative but also quantitative approach of the pollution repartition.

The first objective of this study is to develop a methodology to study the mixed pollutant distribution on solid phases applied to specific urban soils, such as stormwater sediment and former industrial site. The second objective is to study the adsorption/desorption process. The study is organized into steps: selection of specific urban sites, to define a methodology, to establish a method for physical and chemical characterisations, including microscopy observations to localized pollutants in the solid phases, and to implement batch and column experiments in order to model the pollutant release.

This paper presents the results of preliminary sampling of waters and sediments in infiltration basins, the advancement state of the experimental sites selection and proposes a methodology for the study of the mixed pollutants speciation.

MATERIAL & METHODS

Criteria for the choice of sampling sites

The investigation phase focuses on two types of sites, retention/infiltration basins and former craft and/or industrial areas containing both organic and inorganic pollutants.

In large cities, such as Nantes or Lyon, these kinds of sites are common. About 250 infiltration structures have been inventoried in Nantes or in Lyon areas.

Criteria for the choice of retention/infiltration basins are as follows: basins receiving highway runoff waters with a high traffic; size around or greater than 1 ha; containing old and non redisturbed sediments and a secure access.

The industrial site (or former craft), should have an important and well identified waste storage or rejection surface, pollutants should be detected in groundwater, the hydrogeology of the site have to be identified and easy to understand and the most important point is to have the authorization of the exploiting.

Analytical methods

Trace metal analysis in surface water

Surface water were analysed for total trace metals (NF EN ISO 11885). 100 mL of sampling water were acidified by 0.5 of the site have to be identified and easy to understand and the most important point is to have the mL of pure HNO₃ (nitric acid), sonificated during 15 minutes and kept in contact with the acid during 165 minutes. Then, the solution was filtered using a 0.45 μm

Whatman (n°40) filter. The analysis of major and trace elements was performed using an ICP-OES (Inductively Coupled Plasma – Optical Emission Spectrometer) (Varian 720-ES). The quantification limit for As, Cd, Cr, Cu, Ni, Pb and Zn are respectively 6, 0.5, 5, 2, 10, 10 and 2µg/L. In case of concentration under the limit of quantification, the sample was analyzed using an ICP-MS (Inductively Coupled Plasma – Mass Spectrometer) (Varian 820-MS). The ICP-MS limit of quantification for water is ranging from 0.02µg/L to 0.3µg/L depending on the element (Table 1).

Trace metals analysis in sediment

Trace metals were extracted by an acid attack from the sediments collected in infiltration basins (NF X 31-147). 0.5g of sediment is sieved to 2 mm to remove gravel and roots, and calcinated during 3 hours at 450°C. Then, after the addition of 10 mL of HF (hydrofluoric acid) and 3 mL of HClO₄ (perchloric acid), the sample was left to boil dry on a hotplate at 160°C. Once dry, the residue is taken up by 1mL of HNO₃ (nitric acid) at room temperature during 30 min, then 10mL of ultrapure water is added and heated at 60°C for 1h. The residue was transferred into a 100mL flask and filled up with ultrapure water to the mark. This sample was filtered by a 0.45µm Whatman (n°40) filter and analyzed using an ICP-MS (Varian 820-MS) for major and trace elements.

Organic pollutant analysis in sediments

The analyses of total hydrocarbons, PAHs and PCBs were conducted on sediment samples (at IDAC Nantes laboratory). PAHs and PCBs were analyzed using a gas chromatography coupled to a mass-spectrometer (GC/MS (/MS)) according to the XP X33-012 norm. For the total hydrocarbons, the ISO 11046 (X31-410) norm is used and analysis is performed with an Infrared spectrophotometer.

Methodology for studying pollutant speciation

The following methodology is available for both kinds of sites: retention-infiltration basins and industrial areas.

The soil can be regarded as a complex solid matrix, consisting of mineral and organic phases. To locate pollutants in these different phases of the soil, there are two main types of methods: physical methods (or direct), which consist in a non-destructive separation of the soil phases, depending on their physical properties (size, density ...); and chemical methods (or indirect) where the pollutant is taken out of its structural context, by chemical attacks, analyses are indirect insofar as they are done in the solution “CORNU et al. (2000)”.

Physical fractionation

The use of physical fractionation decreases the heterogeneity of the soil, thus chemical analysis of pollutants can be made for each fraction and so indicates the repartition of those pollutants on the soil different phases. One of the fractionation usually studied is the densimetry (fractionation by density of soil phases). “DOELSCH et al (2006)” proposed an original density fractionation, based on a simple preparation, which allows the identification of pollutants in the different density fraction. In addition to quantify the pollutants, this non destructive method allows the identification of the phase structure by using X-ray diffraction, Nuclear magnetic resonance spectroscopy... The main problem encountered is the organomineral aggregation which changes the density of the organic and the mineral phases of the agglomerate.

Chemical extractions

Three types of methods were presented: simple, kinetic and sequential extractions. These methods have been used for speciation of trace metals.

- Simple extractions help to differentiate labile or "available" compartment, from non mobile compartment. Indeed, this simple method is commonly used in soil science in particular to predict the availability of the trace metals for plants. Four types of extraction solutions are mainly used: deionized water (often to simulate natural conditions of soil), saline solutions (mainly CaCl_2 and BaCl_2), diluted acids and organic complex as EDTA or DTPA. Phases extracted by the extraction solution containing the most mobile metals, are potentially the most extractable.
- More complex techniques allow the differentiation of three compartments, the labile, the slightly mobile and immobile (or not extractable). Kinetic extractions are based on simple extractions of trace metals at different contact times by a single extractant (salt or EDTA complexes in most of cases).
- Sequential extractions were developed in the early 1980s. Initially for trace metals speciation in sediments, they have been adapted to soils. The principle is to submit a sample, in order, to a series of increasing strength reagents to solubilise different phases (or fractions) of soil. The various metals associated with these phases or fractions are solubilised at the same time and quantified. Patterns of extractions contained usually four steps (Figure 1). The fractions chosen are those likely to be affected by variations in environmental conditions. The extractant used in the four steps differ from one author to another, but a standard method from the BCR (Bureau Communautaire de Référence) is extensively used (Figure 1).

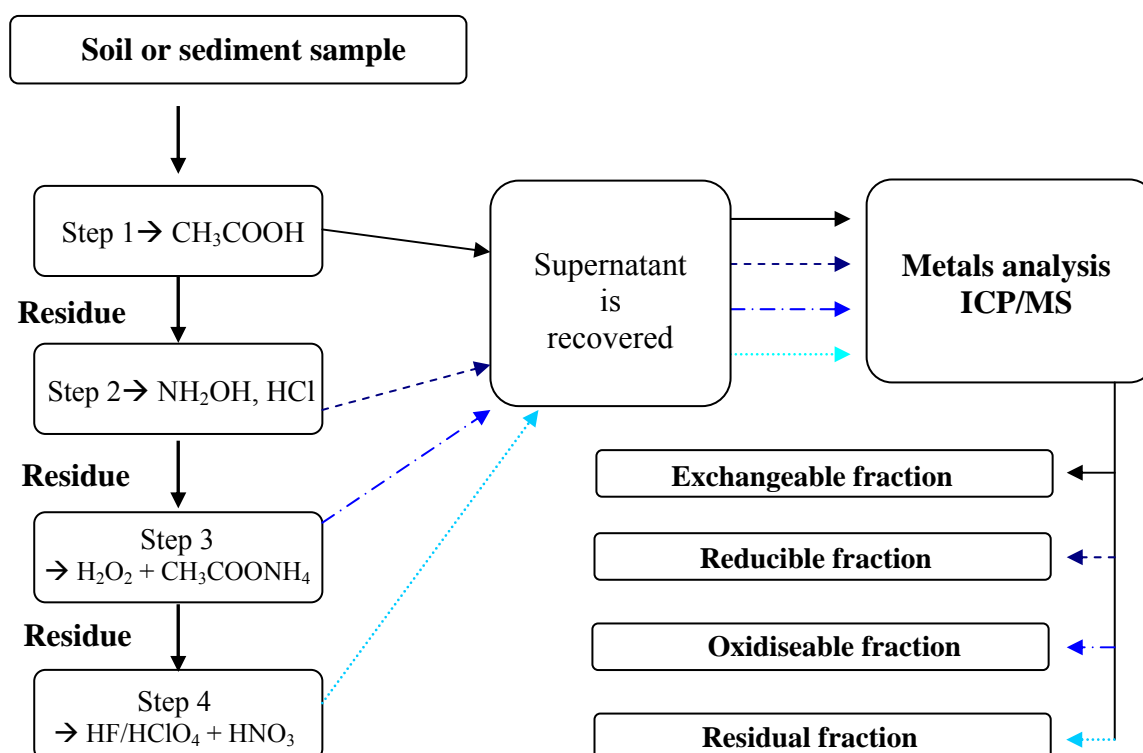


Figure 1: Sequential extraction procedure, according to "JAMALI et al. (2008)"

Chemical fractionation

The chemical fractionation suggested by “DOICK et al (2005)” depends on the chemical proprieties (mainly the solubility). It is a non destructive method which allows the fractionation of humic substances (fulvic acid, humic acid and humin) and also of the mineral phase (Figure 2). Both organic and trace metals remain associated to the different fractions. The original solvent used is the MIBK (Methyl IsoButyl Ketone).

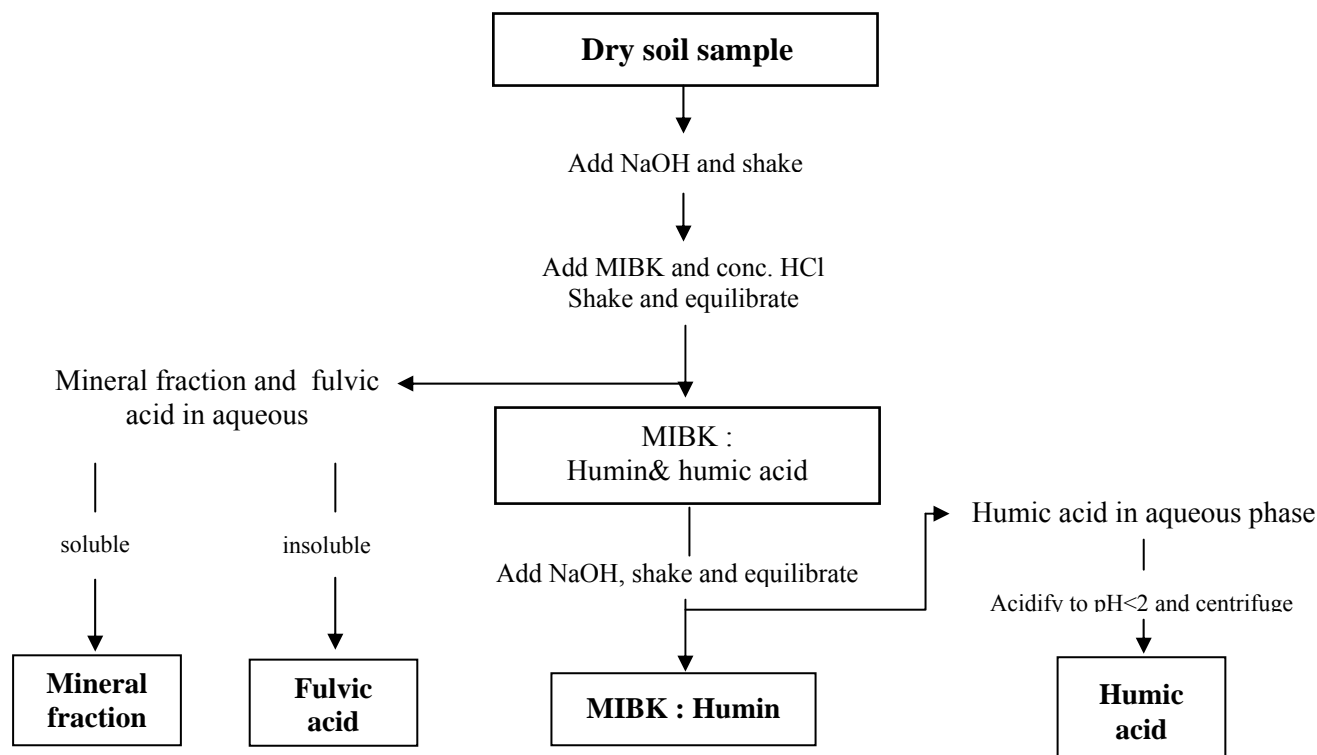


Figure 2: MIBK fractionation procedure, according to “DOICK et al (2005)”

The foreseen methodology

In order to localise pollutants in the different phases of the soil, the previous methods (chemical extraction and fractionation) will be used. Indeed, the chemical extractions procedure will inform us on the mobility of trace metals in the operationally defined fractions. It could be interesting to adapt these methods to the organic compounds.

Furthermore, it will be useful to assemble the physical and chemical fractionations, i.e. to carry out a density fractionation to the mineral fraction resulting from the MIBK fractionation procedure. Then quantification of both the organic and inorganic pollution in all phases will be possible. This by trying to minimize the organomineral aggregations could also be reduced in the density fractionation.

Otherwise, in each case, to follow the separation (in fractionation methods) or the solubilisation (in sequential extractions), we will associate analytical techniques as X-ray diffraction, Scanning or Transmission Electronic Microscopy, Infrared spectrophotometer or X-ray Photoelectron Spectroscopy.

RESULTS AND DISCUSSION

Infiltration basin selection

A first set of experimental sites was selected along the ring-road of Nantes (west of France). Five

retention-infiltration basins receiving highway runoff waters were selected and a preliminary sampling campaign was performed in December 2008 and January 2009 to collect surface water and sediments from a central zone of the basins: along A11 highway (four basins) and next to Nantes ring-road (Cheviré basin) (Figure 3). This last basin has been studied by LCPC since 1991.



Figure 3: Location of the five infiltration basins and the landfill in Nantes area

Sites from the A 11 highway

These basins are located in the east of Nantes (Figure 3), a few kilometers from each other, and are named as follows (from the farther west to the most easterly), Gesvres, Boisbonne, Erdreau and Jouhandière. All have been in use since the opening of the A11 in 1992 and had never been dredged since this date.

Gesvres is on the border between the A11 highway and the Nantes ring-road. It carries an average daily flow of 80 000 vehicles. The overflow of the basin discharges into a stream named Gesvres.

For Boisbonne, Erdreau and Jouhandière, the drained runoff waters only come from the A11 highway. The flow of vehicles is an average of 27 000 per day.

Cheviré basin

This basin is located in the south west of Nantes (Figure 3), it receives runoff waters from 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 drainage surface area

is around 1.9 ha. Runoff waters are collected in gulleys, driven through an aluminium gully and then through a concrete pipe to the basin. The surface of the basin is 0.78 ha and its depth is about 1.5 m. The runoff waters are collected and infiltrated via a single flow path from the entrance to the overflow of the basin to the Loire river.

The basin had not been dredged since 1991, except in a small area close to the main inlet. This results in the settlement of a sedimentary layer whose thickness varies from 5 to 30 cm depending on the location in the basin, laying on a sandy subsoil.

Analytical results

Table 1 summarizes the results of trace metals in surface water for each site. The trace metal concentrations are as follows, As (from 5.10 to 20.52 $\mu\text{g/L}$), Cd (from 0.01 to 2.8 $\mu\text{g/L}$), Cr (from 0.30 to 8.6 $\mu\text{g/L}$), Cu (from 1.03 to 296 $\mu\text{g/L}$), Ni (from 0.92 to 12.4 $\mu\text{g/L}$), Pb (from 0.28 to 80 $\mu\text{g/L}$) and Zn (from 6.10 to 1946 $\mu\text{g/L}$). Cheviré's trace metal concentrations, except for arsenic, are from 2 to 300 times higher than concentrations for the other sites. For arsenic, the values are almost in the same order of concentration. We can also notice that cadmium values for the A11 sites are close the limit of quantification thus negligible.

Table 1: Analytical results for trace metals in surface water for each site

($\mu\text{g/L}$)	As	Cd	Cr	Cu	Ni	Pb	Zn
LQ ⁽¹⁾	0.02	0.02	0.02	0.02	0.05	0.2	0.3
Gesvres	20.52	0.01	0.70	3.39	3.32	0.63	12.55
Boisbonne	7.36	0.05	0.32	2.06	10.67	0.39	34.19
Erdreau	7.92	0.06	0.30	1.98	2.89	0.45	6.10
Jouhandière	5.10	0.02	0.39	1.03	0.92	0.28	10.76
Cheviré	14.1	2.8	8.6	296	12.4	80	1946
Dutch standard ⁽²⁾	50	5	50	1000	50	50	5000

⁽¹⁾ Limit of quantification for the Varian 820-MS ICP/MS

⁽²⁾ Threshold at which a soil is considered contaminated (according to the Dutch standard)

The results of trace metals in sediments for each site are presented in table 2. The trace metal concentration are as follows, As (from 28 to 174 mg/kg), Cd (from 0.3 to 1.3 mg/kg), Cr (from 57 to 97 mg/kg), Cu (from 31 to 411 mg/kg), Ni (from 32 to 76 mg/kg), Pb (from 33 to 271 mg/kg) and Zn (from 125 to 1655 mg/kg). We can notice again that Cheviré's values for copper, lead and zinc are in average respectively 13, 8 and 13 times higher than the other for the extreme values. Nevertheless, for the A11 basins, arsenic concentrations seem to be higher and require intervention. Nickel, chromium and cadmium concentrations were in the same range.

Table 2: Analytical results for trace metals in sediments for each site

(mg/kg)	As	Cd	Cr	Cu	Ni	Pb	Zn
Gesvres	174	1	72	85	41	83	327
Boisbonne	93	1.3	59	70	76	44	410
Erdreau	71	0.3	64	31	38	33	125
Jouhandière	40	0.5	57	51	32	46	465
Cheviré	28	1	97	411	37	271	1655
Polluted soil ⁽¹⁾	29	0.8	100	36	35	85	140
Intervention's threshold ⁽²⁾	55	12	380	190	210	530	720

⁽¹⁾ Value at which a soil is considered contaminated (according to the Dutch standard)

⁽²⁾ Value at which intervention is necessary (according to the Dutch standard)

Trace metals in surface water and in sediments both presented higher concentrations for Cheviré basin than for A11 basins (except for As). This also applied to Gesvres, which have roughly the same traffic. The geochemical background and the highway maps were consulted.

The main difference in the construction between Cheviré and A11 basins lies in their pits (in which the runoff water transits to the basin). In fact, for the A11 basins all the pits are grassy whereas Cheviré pits are all concrete. Consequently, for A11 sites, the hypothesis is that the pollutants infiltrate before the entrance in the basins.

Furthermore, according to the geochemical background, the high arsenic concentration is due to the geochemical background of Nantes region (ranging from 20 to 500 mg/kg in road basin sediments) and can't be due to anthropogenic sources.

On the basis of trace metal concentrations, we decided to carry out the organic pollutant analyses only for Gesvres and Boisbonne sites. Some results are available for Cheviré basin "Durand et al. 2004".

Table 3, presented the concentrations of 10 PAHs from the 16 PAHs recognized as proprietary pollutants by the US-EPA (US Environmental Protection Agency) and the total hydrocarbon values. The other PAHs and the PCBs haven't significant values.

Table 3: Analytical results for PAHs and Hc(tot) in sediments for the following basins

$\mu\text{m/kg}$	Ba-ANT*	Ba-PYR*	Bb-FLA*	Bghi-PL*	Bk-FLA*	CHY*	FLA*	Icd-PYR*	PHE*	PYR*	Hc(tot)* mg/kg
Gesvres	34	51	75	118	51	71	93	75	54	98	246
Boisbonne	59	74	103	133	74	108	128	96	83	135	997
Cheviré⁽¹⁾	-	-	-	-	-	-	670	-	313	1223	7000
Dutch standard⁽²⁾	20	20	-	20	25	20	15	25	45	-	-

⁽¹⁾ Results from Durand's thesis (2003).

⁽²⁾ Dutch standard applied to a soil containing 25% clay and 10% organic matter

* Abbreviations: Benzo(a)anthracene (Ba-ANT), Benzo(a)pyrene (Ba-PYR), Benzo(b)fluoranthene (Bb-FLA), Benzo(ghi)perylene (Bghi-PYR), Benzo(k) fluoranthene, Chrysene (CHY), Fluoranthene (FLA), Indeno(1,2,3-cd)pyrene(Icd-PYR), Phenanthrene (PHE), Pyrene (PYR) and total hydrocarbons (Hc(tot)).

The three sites are contaminated by hydrocarbons (including PAHs). Gesvres and Boisbonne have a greater variety of PAHs even if they are less concentrated. As for trace metals, the Cheviré concentrations of fluoranthene, phenanthrene, pyrene and the total hydrocarbons are 5 to 10 times higher than the others, the results for Boisbonne are higher than Gesvres, although this was not always the case previously for trace metals.

Site choice

According to the pollutant results, Cheviré and Boisbonne are obviously the selected sites for the following methodology, even if Boisbonne doesn't show high concentration compared to Cheviré.

Industrial sites selection

The BRGM (the French Geological Survey) identified several sites in the Nantes region, based on results of BASIAS and BASOL (DRIRE) data bases.

A visit of the landfill of "Prairie de Mauve" near Nantes (Figure 3) has been organized, but the heterogeneity of the site was such that a pre-study should be done before the selection. This pre-

study consists in searching a delimited area in the landfill in which the heterogeneity is lower and the hydrogeology easier to understand and will be performed by the BRGM.

In addition, negotiations with an industrial operator are in progress for another site. According to the BRGM' census, this site is interesting in terms of mixed pollution.

Cheviré basin previous results

On Cheviré basin, pollutants and sediments speciation have been studied by “DURAND (2003)”. These speciation consisted in the characterisation of the sediment regarding the mineral and organic phases with several analytical techniques, and in following the pollutant mobility with extraction method.

The XRD composite sample results show a fairly uniform pattern, with crystalline phases that are mostly primary silicates (albite, clinocllore, microcline, muscovite and quartz). These results are confirmed by the Scanning Electron Microscopy (SEM) coupled to an Energy Dispersive X-ray (EDX) spectroscopy.

The organic phases have been studied with the IHSS (International Humic Substance Society) protocol, which separates humic substances themselves identified with NMR (Nuclear magnetic resonance spectroscopy), Infrared spectroscopy or GC-MS (Gas chromatography-mass spectrometry). Humic acid represents 57.6% of total organic matter, fulvic acid 4.5%, humic acid 18% and lipids 19.9%. It should be noted that in this protocol, it seems that the humic fraction contains mineral phases.

The mobility of trace metals has been followed within the IHSS protocol for the organic matter and with sequential extractions for the different sediment phases. The following observations have been noted: Cd, Pb and Zn are mainly in fulvic acids fraction, Ni and Cr are mainly in humic fraction, Cu in both humic acid and fulvic acid fractions, furthermore, Cd and Zn are located in the exchangeable fraction (of the sequential extractions), Ni and Cr are in the residual fraction and Cu and Pb are bond to the organic fraction.

Our new methodology should go beyond these conclusions. In fact, we should be able to localise more precisely both organic pollutants and trace metals in all the soil phases by proceeding to the MIBK extraction with the densimetric fractionation. The obtained results will be compared to sequential extractions for the trace metals. Additionally, we will observe and characterise the soil phases with several technical's analysis as XPS (X-ray Photoelectron Spectroscopy), μ -XRF (X-ray Fluorescence micro-analyzers) which should give more information on pollutant speciation.

CONCLUSIONS

For the site research, two retention/infiltration basins have been selected (Cheviré and Boisbonne), however, investigation continues, we are looking for an industrial site and other retention-infiltration basins containing both organic and inorganic pollutants. In fact, the study of several sites will be useful to compare and validate our results.

The new methodology will be applied on the Cheviré and Boisbonne sediments; it will be extended to the future sites.

Finally it could be very interesting to establish a correlation between a given pollutant and the abundance of a particular phase. This would allow the development of simple indicators based on soil type obtained with simple analytic techniques which would have been validated by more complicated techniques.

Furthermore, these results should give information for the choice of the future modelling parameters.

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