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Evolution of metals and their chemical forms in land-disposed dredged marine sediments

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Abstract:

Land disposal is a treatment which has been considered in the framework of the SEDI.MAR.D. 83 project in order to decrease chemical contamination of dredged marine sediments. Natural aging could involve physico-chemical and/or biological transformations in the sediments resulting in a modification of its toxicity. This study was carried out to better understand the fate of metals and their chemical forms during this treatment.

A degradation rate of 50% was observed after two months of land disposal for tributyltin (TBT) which is one of the most dangerous organotin compounds. This degradation is accompanied with the formation of less dangerous species such as dibutyltin and monobutyltin. For arsenic, only inorganic forms were identified (As(III) and As(V)) with a change in their distribution as a function of the time of land disposal. A decrease of As(III) in favour of As(V) with time was shown. This oxidation was also observed for chromium with the formation of small amounts of hexavalent chromium. Because of its high toxicity, the formation of Cr(VI) can limit the duration of land disposal. It seems therefore preferable to consider a short time of land disposal allowing degradation of TBT while minimizing Cr(VI) formation. As no really efficient treatment exists for the moment to manage contaminated dredged sediments, this study shows that land disposal could be considered as a first and non expensive approach. If the amount of contamination is sufficiently decreased by this process, it could be possible to consider sediment valorisation in the field of public works for example.

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1. Introduction

The SEDI.MAR.D. 83 project has been initiated by the Conseil Général du Var (France) in order to establish and evaluate different scenarii for the management of dredged marine sediments. Among the different treatments studied in this project, land disposal in confined facilities has been considered because it could allow a decrease of sediment toxicity by natural attenuation. Sediment aging can generate chemical, physical and/or biological transformations which could transform the structure of some toxic molecules into less dangerous compounds. Land disposal has already shown its efficiency for organic molecules such as Polycyclic Aromatic Hydrocarbons (AMIR *et al.*, 2005; VERMEULEN *et al.*, 2007) but no work has been performed to better understand the behaviour of chemical forms of metals during the aging process of marine sediments land disposed.

The metals content being important in some sediments from the Mediterranean sea, their behavior as well as those of their chemical species has been studied in freshly dredged sediments land disposed during ten months. Only the total metal concentrations are taking into account in risk assessment studies dealing with land disposal of sediments and it is generally considered that mobility of metals increases with sediment aging due to the oxidation of anoxic sediments (CAILLE *et al.*, 2003; CAPPUYNS *et al.*, 2006). However, this behaviour was only studied for river sediments and remains poorly known for marine sediments.

Furthermore, low information is available about changes in the chemical species of metals during sediment aging. Speciation analyses allowing to reach this information can be interesting because it will be possible to well characterise dredged materials but also to better understand and assess the different environmental issues associated with land disposal of sediments. For example, it is well known that mineral tin is harmless but organotin compounds such as butyltin species are very toxic, the toxicity increasing with the number of butyl groups (CRAIG, 1986). Because of its biocide properties, tributyltin (TBT) has been intensively used in antifouling paints during the last two decades. Despite the ban on using these paints, TBT and its degradation compounds such as dibutyltin (DBT) and monobutyltin (MBT) remain in dredged marine sediments (ALZIEU, 2000). Mercury in sediments is generally present as inorganic but this element is strongly affected by methylation/demethylation processes that will determine the fate of Hg species and thus its toxicity. Microbial methylation is one of the major process which transforms inorganic mercury into more toxic methylmercury (MeHg) which is easily bioaccumulated and bioamplified along the food chain (CRAIG, 1986). Knowledge of evolution of arsenic species during this treatment is also of importance because land disposal could transform the toxic inorganic species of arsenic (As(III) and As(V)) into less dangerous organic species (e.g. MMA, DMA, AsB) (O'NEILL, 1995). In sediments, chromium can be present as trivalent chromium (Cr(III)) and hexavalent chromium (Cr(VI)). If Cr(III) is essential, Cr(VI) is classified as a carcinogenic compound (KRETCHIK, 2005). Only speciation analyses can give information about the toxicity related to chromium in sediments.

Monitoring of chemical species of some elements of importance in dredged marine sediments land disposed over a long period seems therefore to be a good approach to better assess the fate and the toxicity of metals in sediments. Thus, the aim of this study is to estimate the transformation of metal species in dredged marine sediments disposed to land in real environmental conditions.

2. Material and methods

2.1 Land disposal of sediments

Treatments applied to the sediments at the pilot site of SEDI.MAR.D. 83 is summarized in figure 1.

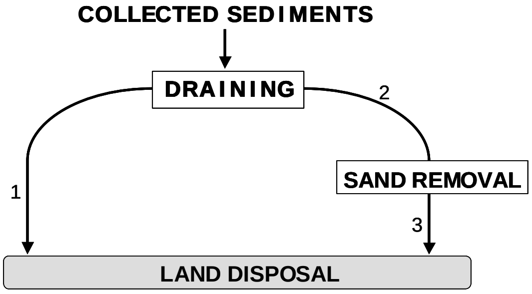

Figure 1. In situ treatments applied to the sediments.

After dredging of different harbours of the Provence Alpes Côte d'Azur (PACA) region (France), the collected sediments were transported at the pilot site located in La Seyne-sur-Mer (France). They were first stored in a watertight settling tank where leaching waters have been collected and then treated before discharge into the sea. Then, a part of the drained sediments was stored on the watertight platform without other treatments (raw sediments) (way 1, figure 1). Sand was removed in the other part of the sediments (way 2, figure 1) to separate fines that concentrate contaminants from the less contaminated sand fraction. After sand removal, sediments were disposed to land (sand free sediments (way 3, figure 1). Sediments were stored on this platform for a period of ten months where they were regularly humidified, and turned once a week to enhance oxygenation. Sediments were sampled every two months over the 10 months to monitor the levels of metals as well as some of their species. Sampling under an inert atmosphere was impossible to perform for technical reasons. About 1 kg of sediments was collected at different places along the sediment land disposal to obtain a representative sample. After sampling, sediments were immediately stored at –18°C to stop their reactivity.

2.2 Analytical procedure

Parameters determined in the dredged sediments (raw and sand free sediments) are the total contents of Ni, As, Sb, Cd, Sn, Se, Hg, Pb, Mn, Zn, Cr, Cu, Fe and Al as well as the chemical species of As, Cr, Sn and Hg. The analytical procedure applied to the sediments is presented in figure 2. Each time it was possible, quality of the analysis has been controlled by measurement of certified reference materials.

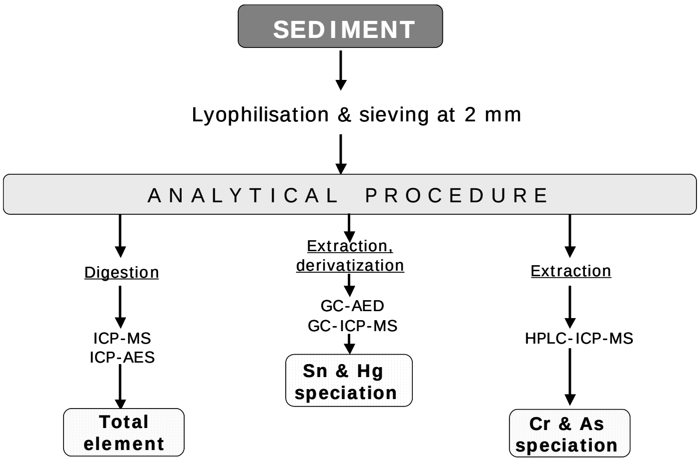

Figure 2. Analytical procedures applied to the sediments.

Technical details about the different analyses are available in other work (SEBY *et al.*, 2007; DIRKX *et al.*, 1994; RODRIGUEZ MARTIN-DOIMEADIOS *et al.*, 2003; THOMAS *et al.*, 1997; SEBY *et al.*, 2003). Total metal analysis were performed by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) (Ni, As, Sb, Cd, Sn, Se, Hg, Pb) or Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) (Mn, Zn, Cr, Cu, Fe et Al) after microwave digestion (closed system) in presence of nitric and hydrofluoric acids. Chemical species of some elements have been determined with coupled techniques associating on-line a chromatographic separation (gas or liquid chromatography) and a spectrometric detection. Organotin compounds were determined after microwave extraction in presence of acetic acid. To transform extracted organotin compounds in a volatile form which is analyzable by gas chromatography, a derivation was performed before analysis by Gas Chromatography – Atomic Emission Detection (GC-AED). Mercury species were determined by Inductively Coupled Plasma Mass Spectrometry (GC-ICP-MS) after microwave extraction in HNO_3 6M followed by ethylation (derivation step).

Arsenic and chromium speciation analysis have been performed with High Performance Liquid Chromatography - Inductively Coupled Plasma Mass Spectrometry (HPLC-ICP-MS). In both cases, separation is achieved using an anionic exchange separation mechanism. For arsenic species, extraction is performed with phosphoric acid 1M with a microwave heating. For chromium, an alkaline extraction was done (NH_4^+/NH_3 buffer solution at pH 9) in an ultrasonic bath. Such conditions only allow hexavalent chromium extraction, trivalent chromium precipitating at this pH.

3. Results and Discussion

3.1 Evolution of the total metal concentrations with the time of land disposal

For most elements considered in this study, concentration values in the sediments are very often higher than the GEODE levels. These levels were established to give references to decision makers engaged in dredged marine sediments management. Two different concentration levels (N1 and N2) have been defined to characterize the quality of a sediment. N1 is the level under which dumping at sea is authorized and N2 is the level above dumping at sea is not allowed. Between N1 and N2, a complete characterization of the sediment is necessary. In the sediments studied herein, the As, Cd, Hg, Pb, Zn and Cu concentrations are higher to the N2 level but the other elements are not mentioned by GEODE. Dumping at sea is then forbidden and this sediment has to be considered as a dangerous waste.

For sand free sediments, metal concentrations remain nearly constant during 10 months whereas a decrease is observed for the raw sediments with obtention of a plateau after 4 months of land disposal. This decrease is particularly significant during the first two months and becomes more progressive after. Taking into account measurement uncertainties, concentrations can be considered as stable between the fourth and the tenth month for most elements. Concentration values remain however high after ten months and are still superior to the N2 level. For major elements such as Fe, Mn and Al, two different behaviors can be differentiated. Whereas iron and aluminium have levels that decrease according to the trends observed for trace elements, the decrease of manganese concentrations is lower during the first two months (only 15%) and remains stable after. Total organic carbon follows the evolution observed for iron and aluminium; 20 % decrease during the first two months and stabilization after.

From these results, it seems that a period from two to four months is necessary to oxidize the freshly dredged sediments. This behavior is less significant for sand free sediments because the sand removal treatment itself produces a fast oxidation and therefore, the metal concentrations remain stable during land disposal.

The more important concentrations found in sand free sediments compared to raw sediments can be explained by the poor affinity of metals for sand. Only arsenic presents very close concentration in both types of sediments. This element is therefore not influenced by the presence of sand, suggesting a similar affinity of arsenic with all types of particles.

It was already shown that the changes in redox conditions affecting metal associations operate on a much shorter time-scale than one year (SINGH *et al.*, 1998). Dewatering and oxidation of sediments initially in anoxic conditions occur during the first two weeks. During this period, the metals that were initially present as insoluble gradually become available (STEPHENS *et al.*, 2001). Indeed, the partitioning of these elements in anoxic sediments is generally dominated by the formation of metal sulfides (CAILLE *et al.*, 2003; CAPPUYNS *et al.*, 2006). Mercury and copper may also be present in important concentration in the structure of pyrite (CAILLE *et al.*, 2003). Besides, large quantities of organic matter do generally accumulate in anoxic sediments due to the fact that microbial activity is reduced in oxygen-poor environments. These natural organic compounds are also frequently considered as sinks for metallic pollutants. As a consequence, it is now generally recognised that oxidation of dredged material can lead to a modification of the metal mobility (CAILLE *et al.*, 2003; CAPPUYNS *et al.*, 2006; STEPHENS *et al.*, 2001). It was however shown that solubility of metals increased rapidly during the early stages of aeration but was then followed by a fast readsorption, minimising mobility (CAILLE *et al.*, 2003).

3.2 Evolution of organotin compounds with the time of land disposal

Butyltin concentrations during the 10 months of land disposal is presented in figure 3 for raw sediments. The same profile was obtained for sand free sediments.

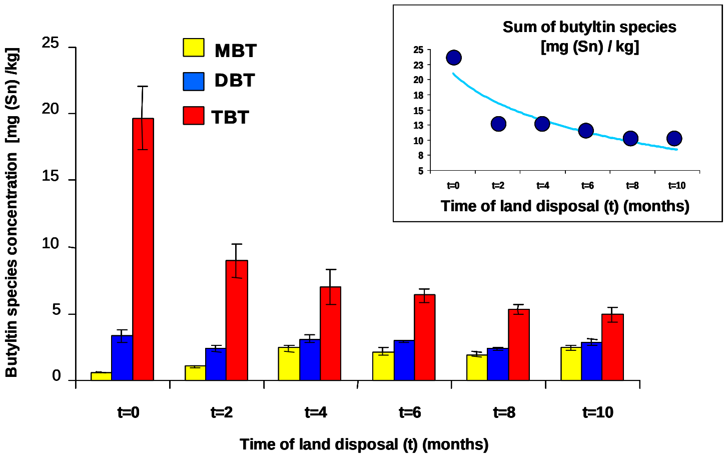

Figure 3. Evolution of butyltin concentrations with the time of land disposal.

Butyltin species concentrations determined in sediments show a TBT concentration twenty times higher than the N2 level recommended by GEODE. These values totally prevent dredged sediments from dumping at sea.

Independently from the type of sediments, a decrease of the TBT concentrations is observed in figure 3. This can be explained by the natural degradation of TBT into DBT, MBT and then inorganic tin. DBT decreases after two months of land disposal and is stable after. This DBT increase is therefore probably due to TBT degradation. MBT significantly increases during land disposal because of the uptake due to DBT degradation.

The profile of TBT as the function of the time of land disposal (figure 3) is very similar to what has been observed for most trace elements with an important decrease of the concentrations during the first two months and stabilization after. TBT degradation is fast during the two first months with a loss of half of the initial concentration. The kinetic of TBT degradation is slower after. The fast oxidation of the anoxic dredged sediments allows thus degradation of the most dangerous butyltin compound. After two months, the sedimentary mass being totally oxidised, only the microbial degradation plays a role in the fate of TBT.

TBT degradation has already been shown in soils (HEROULT *et al.*, 2008) and sediments (SARRADIN *et al.*, 1995; TESSIER *et al.*, 2007). Organotin compounds degradation can be produced by abiotic processes (temperature, light irradiation, organic or inorganic catalysts, redox conditions) but the biological way is considered as the most significant process (TESSIER *et al.*, 2007). Degradation is clearly identified as a successive loss of a butyl group. According to different studies, TBT half-lives values in sediments are short (32 days in a model freshwater ecosystem (TESSIER *et al.*, 2007) and close to 80 days in a spiked soil (HEROULT *et al.*, 2008). Half-lives of TBT have also been calculated in marine sediment cores considering a depth corresponding to a 14 years period. In these anoxic conditions, half-life of TBT is close to 2.1 years (SARRADIN *et al.*, 1995). Therefore, TBT degradation seems favored in aerated conditions and degradation of half of the initial TBT can be obtained in some months.

3.3 Evolution of mercury compounds with the time of land disposal

Mercury being present at high levels, the determination of Hg species can be interesting for a better evaluation of the toxicity of the sediments. Mercury in dredged sediments is probably initially present as inorganic (e.g. sulfides) but could be transformed into methylated species by the microbial activity that increases with the time of land disposal. However, analyses by GC-ICP-MS have shown methylmercury concentrations lower than 1 µg kg^{-1}. Therefore mercury remains as inorganic during the 10 months of land disposal.

3.4 Evolution of arsenic compounds with the time of land disposal

Although the total arsenic concentration is not influenced by the presence of sand or the duration of the land storage, changes in the distribution of As species can occur. Such changes are important to identify because toxicity and mobility of arsenic is strongly linked to its chemical form.

Only inorganic species of arsenic were detected in sediment extracts. The absence of As methylated species such as DMA or MMA shows the low methylation activity of the sediments, even after 10 months land storage. Changes in the distribution of inorganic As species were however observed; results are given in figure 4.

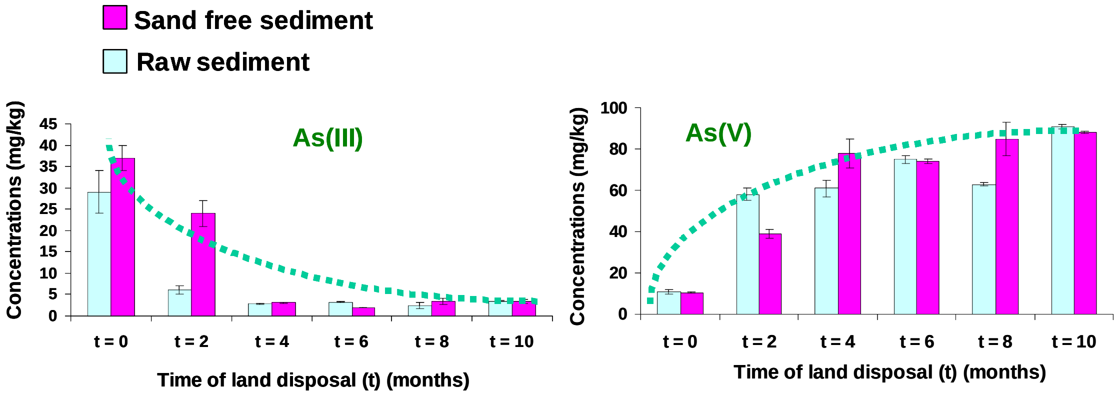

Figure 4. Evolution of As(III) and As(V) in sediments with the time of land disposal.

Figure 4 shows a decrease of the As(III) concentration with sediment aging and an increase of As(V) at the same time. When examining the experimental results, the sum of extracted As species is lower than total arsenic found in the sediments. At t=0, the sum of extracted species only represents 25% of total As in the raw sediments, recoveries increase up to 44% to reach 80% at the end of land disposal. Thus reducing conditions that prevail during the first months of land disposal favor the presence of As(III) which is present in relatively insoluble bearing phases. With sediment aging, As(V) becomes predominant and then more quantitative recoveries are obtained showing that As(V) is present in more soluble solid phases than As(III).

In the initial redox conditions of the dredged sediments, arsenic is probably present in sulfide and iron based minerals (O'NEILL, 1995; BOSTICK *et al.*, 2004). Oxidation with time of land disposal allows release of this reduced fraction of As to give As(V). As(V) can then form stable solid minerals by precipitation with divalent cations such as Ca, Fe, Mn, Ni or Pb (O'NEILL, 1995) or be retained by sorption on some solid mineral phases such as Fe, Al or Mn oxides (XU *et al.*, 1988). As(V) is generally considered as mobile but its mobility can be affected by several physicochemical parameters.

3.5 Evolution of hexavalent chromium with the time of land disposal

The Cr(VI) concentrations determined in sediments land stored during 10 months are presented in figure 5.

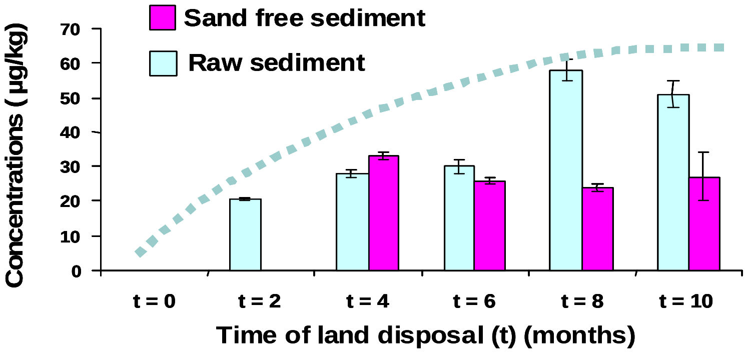

Figure 5. Cr(VI) concentration in dredged marine sediments with time of land disposal.

Whereas no Cr(VI) is detected in freshly dredged sediments, trace amounts are present after 2 months in raw sediments and after 4 months in sand free sediments. The very low concentrations determined explain variability in the results but the formation of Cr(VI) seems stabilised after 4 months. This behaviour is very similar to that obtained for arsenic confirming a global oxidation of the sediments that occurs in the first two months after dredging. Chromium is initially present under the trivalent chromium reduced form and is slowly oxidised into Cr(VI). It was shown that Cr(VI) is not stable in anoxic sediments, particularly if the sulfide fraction identified as acid volatile sulfides is important (RIFKIN *et al.*, 2004; GRAHAM *et al.*, 2009). Cr(III) is then present in refractory mineral phases weakly accessible for oxidation. This could explain why the measured Cr(VI) concentrations are very low compared to the total Cr concentration (close to 100 mg kg^{-1}). This low efficiency of Cr(III) oxidation decreases the environmental risk associated with the presence of Cr in land disposed sediments.

4. Conclusion

This work, initiated in the framework of SEDI.MAR.D 83, has been carried out to better understand the behaviour of contaminants during land disposal of dredged marine sediments. Concentrations of some metals are high and their decrease with sediment aging is not really significant. Changes were however observed for chemical forms of some elements such as Sn, Hg, As and Cr. A significant decrease of tributyltin was showed with the time of land disposal. The degradation of TBT into less dangerous butylated forms shows the great interest of land disposal to decrease the toxicity of dredged sediments.

No methylated species of mercury or arsenic has been detected during this treatment showing the low methylating activity of the studied sediments. Only inorganic species of arsenic are present and a change in their distribution was observed with time. The As(III) concentrations decrease whereas the As(V) contents increase. This oxidation was also observed for chromium with the formation of Cr(VI) after 2 months of land disposal. Hexavalent chromium formed is however very low compared to the total chromium concentration and then does not seem to represent an important environmental risk.

Finally, results obtained herein show the great interest of land disposal as a first cost-effective approach for treatment of marine dredged sediments. This decontamination process however needs a reliable chemical monitoring to optimise the duration of land disposal before valorisation. It would be now interesting to better assess evolution of organic compounds for an optimised management of sediments.

5. References

ALZIEU C. (2000). *Environmental impact of TBT: The French experience*, Science of the Total Environment, Vol. 258, pp 99-102.

AMIR S., HAFIDI M., MERLINA G., HAMDI H., REVEL J.C. (2005). *Fate of polycyclic aromatic hydrocarbons during composting of lagooning sewage sludge*, Chemosphere, Vol. 58, pp 449-458.

BOSTICK B.C., CHEN C., FENDORF S. (2004). *Arsenic retention mechanisms within estuarine sediments of Pescadero, CA*, Environmental Science & Technology, Vol. 38, pp 3299-3304.

CAILLE N., TIFFREAU C., LEYVAL C., MOREL J.L. (2003). *Solubility of metals in an anoxic sediment during prolonged aeration*, Science of the Total Environment, Vol. 301, pp 239-250.

CAPPUYNS V., SWENNEN R., DEVIVIER A. (2006). *Dredged river sediments: potential chemical time bombs ? a case study*, Water, Air & Soil Pollution, Vol. 171, pp 49-66.

CRAIG P.J. (1986) Organometallic compounds in the environment. Longman, London, 415 p.

DIRKX W.M.R., LOBINSKI R., ADAMS F.C. (1994). *Speciation analysis of organotin in water and sediments by gas chromatography with optical spectrometric detection after extraction separation*, Analytica Chimica Acta, Vol. 286, pp 309-318.

GRAHAM A.M., WADHAWAN A.R., BOUWER E.J. (2009). *Chromium occurrence and speciation in Baltimore harbour sediments and porewater, Baltimore, Maryland, USA*, Environmental Toxicology and Chemistry, Vol. 28, pp 471-480.

HEROULT J., NIA Y., DENAIX L., BUENO M., LESPES G. (2008). *Kinetic degradation processes of butyl- and phenyltins in soils*, Chemosphere, Vol. 72, pp 940-946.

KRETCHIK J.T. (2005). *OSHA's direction*, Chemical Health & Safety, Vol. 12, pp 44-44.

O'NEILL P. (1995). *Arsenic*. Dans: Heavy metals in soils, Blackie Academic & Professional, London, pp 105-121.

RODRIGUEZ MARTIN-DOIMEADIOS R.C., MONPERRUS M., KRUPP E., AMOUROUX D., DONARD O.F.X. (2003). *Using speciated isotope dilution with GC-inductively coupled plasma MS to determine and unravel the artificial formation of monomethylmercury in certified reference sediments*, Analytical Chemistry, Vol. 75, pp 3202-3211.

RIFKIN E., GWINN P., BOUWER E. (2004). *Chromium and sediment toxicity*, Environmental Science & Technology, Vol. 38, pp 267A-271A.

SARRADIN P.M., LAPAQUELLERIE Y., ASTRUC A., LATOUCHE C., ASTRUC M. (1995). *Long term behaviour and degradation kinetics of tributyltin in a marina sediment*, The Science of the Total Environment, Vol. 170, pp 59-70.

SEBY F., BENOIT-BONNEMASON C., DONARD O.F.X. (2007). Evolution des métaux et de leurs formes chimiques dans des vases portuaires dans le cadre d'un stockage à terre. Rapport de contrat SEDI.MAR.D. 83, 49 p.

SEBY F., GAGEAN M., GARRAUD H., CASTETBON A., DONARD O.F.X. (2003). *Development of analytical procedures for determination of total chromium by quadrupole ICP-MS and high-resolution ICP-MS, and hexavalent chromium by HPLC-ICP-MS, in different materials used in the automotive industry*, Analytical Bioanalytical Chemistry, Vol. 377, pp 685-694.

SINGH S.P., TACK F.M., VERLOO M.G. (1998). *Heavy metals fractionation and extractability in dredged sediment derived surface soils*, Water, Air and Soil Pollution, Vol. 102, pp 313-328.

STEPHENS S.R., ALLOWAY B.J., PARKER A., CARTER J.E., HODSON M.E. (2001). *Changes in the leachability of metals from dredged canal sediments during drying and oxidation*, Environmental Pollution, Vol. 114, pp 407-413.

TESSIER E., AMOUROUX D., MORIN A., LEHNOFF C., THYBAUD E., VINDIMIAN E., DONARD O.F.X. (2007). *(Tri)Butyltin biotic degradation rates and pathways in different compartments of a freshwater model ecosystem*, The Science of the Total Environment, Vol. 388, pp 214-233.

THOMAS P., FINNIE J.K., WILLIAMS J.G. (1997). *Feasibility of identification and monitoring of arsenic species in soil and sediment samples by coupled high-performance liquid chromatography - Inductively coupled plasma mass spectrometry*, Journal of Analytical Atomic Spectrometry, Vol. 12, pp 1367-1372.

VERMEULEN J., VAN GOOL M.P.M., MENTINK G.H., JOZIASSE J., BRUNING H., RULKENS W.H., GROTENHUIS J.T.C. (2007). *Biochemical ripening of dredged sediments. Part 2. Degradation of polycyclic aromatic hydrocarbons and total petroleum hydrocarbons in slurried and consolidated sediments*, Environmental Toxicology and Chemistry, Vol. 26, pp 2540-2549.

XU H., ALLARD B., GRIMVALL A. (1988). *Influence of pH and organic substance on the adsorption of As(V) on geologic materials*, Water, Air & Soil Pollution, Vol. 40, pp 293-305.