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**Development and application of a methodology for screening, on the basis of the carcinogenic (H7), toxic for reproduction (H10) and mutagenic (H11) criteria of the latest European legislation, hazardous vs. non-hazardous sediments to be disposed of on land**

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► **To cite this version:**

Christophe Mouvet. Development and application of a methodology for screening, on the basis of the carcinogenic (H7), toxic for reproduction (H10) and mutagenic (H11) criteria of the latest European legislation, hazardous vs. non-hazardous sediments to be disposed of on land. *Journal of Soils and Sediments*, 2011, 11 (7), pp.1292-1307. 10.1007/s11368-011-0404-x . hal-00681123

**HAL Id: hal-00681123**

**<https://brgm.hal.science/hal-00681123>**

Submitted on 21 Mar 2012

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3 **Development and application of a methodology for screening, on the basis of the carcinogenic (H7), toxic**  
4 **for reproduction (H10) and mutagenic (H11) criteria of the latest European legislation, dredged sediments**  
5 **to be disposed of on land**  
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11 Received: 14 October 2010 / Accepted: ## June 2011

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13 © Springer-Verlag 2011  
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16 Responsible editor: Sabine Apitz  
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### 35 Abstract

36 **Purpose** According to the European List of Wastes, dredged sediments are either hazardous or non hazardous  
37 waste. Our first purpose was to develop a methodology for applying the criteria H7 (Carcinogen, C), H10 (toxic  
38 for reproduction, R) and H11 (mutagenic, M) of EU Legislation to the results of Routine Sediment Monitoring  
39 Networks - RSMNs. Criteria H7, H10 and 11 are the only ones for which quantitative data are available in  
40 RSMNs. The second purpose was to apply, with a perspective of sediment management, the methodology to data  
41 sets from RSMNs.  
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45 **Materials and methods** The data sets held up to 4,012 inland and 1,362 marine sediments for trace elements,  
46 and up to 2,774 inland and 952 marine sediments for organic micropollutants. Based on i) the trace elements  
47 analysed in RSMNs, ii) a literature review of aqueous solubility of the dangerous inorganic substances (EU list),  
48 and iii) a literature review of trace elements speciation in sediments, twelve inorganic dangerous substances with  
49 CRM properties were selected. For each substance, the threshold concentrations corresponding to a hazardous  
50 waste were then transformed into threshold total trace element contents. For the organic micropollutants, the list  
51 of dangerous substances considered was imposed by the content of RSMNs data bases, and the threshold values  
52 were directly taken from the waste regulation. The statistical distributions of the data set values were then  
53 compared to the threshold values.  
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1 **Results and discussion** Exceedances of the threshold values were observed for all trace elements and were  
2 examined more closely by taking into account i) the relative contribution of the carbonates or sulphides fractions  
3 and ii) for the dangerous substances containing 2 trace elements (Pb & As, Pb & Cr, Zn & Cr), the observed  
4 ratios of the concentrations of the 2 elements compared to the ratios that would be observed if the trace  
5 element(s) was(were) present solely as the dangerous substances considered. Overall, only 0.08% of the samples  
6 may pose a CRM hazard due to their content in Ni, 0.2% for Cd, 0.26% for Cr, and 0.09% for Zn. The highest  
7 concentration of organic contaminant with CRM properties (62 mg/kg, benzo(a)pyrene) remains 16 times below  
8 the corresponding threshold value.

9 **Conclusions** No CRM hazard results from the organic dangerous substances analysed in RSMNs. For the  
10 dangerous inorganic substances holding trace elements analysed in RSMNs, the possibility of CRM hazard  
11 exists at most for 0.6% of the samples considered. Taking into account the H7, H10 and H11 criteria in the  
12 assessment of the possible hazard caused by dredged sediments analysed in RSMNs will not influence the  
13 possible management options for 99.4% of these materials.

14 **Keywords** Carcinogenic (H7) • EU Directive on wastes • Mutagenic (H11) • Sediment • Toxic for reproduction  
15 (H10)

## 16 **1 Introduction**

17 Nowadays, the increased awareness of the need for sustainable development leads many nations to direct their  
18 transportation policies to more environmentally friendly means, like inland water transport. For instance, the  
19 French nationwide consultation on sustainable development (“Le Grenelle de l’Environnement”), involving all  
20 stakeholders, identified transport as an area where major improvements can be achieved, notably through the  
21 promotion of marine and fluvial transport (Le Grenelle 2007; Assemblée Nationale 2008). As a result, dredging  
22 of waterways required to increase the depth and to keep the channels navigable will gain in importance, as will  
23 the amounts of dredged sediments to be managed (Torres et al. 2009).

24 Dredged sediments are typical “mirror entries” of the European List of Wastes (European Commission, 2000):  
25 they are either hazardous or non hazardous, depending on a series of criteria, including their possible  
26 carcinogenic (H7), toxic for reproduction (H10) and mutagenic (H11) character (European Commission, 2008).  
27 The H14 criterion (ecotoxicity) is not considered here since i) there is no standardised battery of ecotoxicity tests  
28 for wastes at EU level and ii) data on ecotoxicity in Routine marine and inland Sediment Monitoring Networks –  
29 RSMNs are extremely sparse. Whether dredged sediment is classified as a hazardous or not hazardous waste is  
30 of major concern for its later management. Hazardous wastes have to be treated or/and stored in specialised  
31 waste disposal facilities (with added cost), whereas non hazardous wastes may be re-used (possible income,  
32 Cornelis et al 2006).

33 The first purpose of this paper was to develop a methodology for applying the H7, H10 and H11 criteria in the  
34 case of sediments likely to be dredged and disposed of on land. These criteria (the only ones for which  
35 quantitative data are available in RSMNs) were chosen as part of the overall assessment of environmental  
36 hazards (including human health) that may be caused by the management of dredged sediments.

1 The second purpose was to apply the methodology to extensive and intensive data sets from French and Belgian  
2 routine monitoring programs of inland and marine sediments, and to assess the implications of this application in  
3 terms of management options of dredged sediments.  
4

## 5 **2 Material and methods**

### 6 **2.1 Data sets available and statistical analysis**

7 Six data sets were examined: the year 2007 campaign of the French Surveillance Control Monitoring Network  
8 (FSCMN) set up in compliance with the European Union Water Framework Directive, the October 2005 through  
9 March 2008 samplings of the French navigable waterways (FNW; Northern, Eastern and Central France), the  
10 March 1998 through August 2007 samplings of the Walloon navigable waterways (WNW), the September 2001  
11 through August 2008 samplings of the Walloon non-navigable waterways (WNNW), the year 1993 through  
12 2005 samplings of the French National Network of Observation of Marine Environment Quality (RNO), and the  
13 March 1998 through May 2008 samplings of the National network of Monitoring of Marine Harbours (REPOM).  
14 The data sets VNF, WNW and REPOM hold samples originating from areas severely impacted by ancient and/or  
15 present industrial activities.  
16

17 The data on trace elements (As, Cd, Co, Cr, Ni, Pb, Zn) from FSCMN, FNN, WNW and WNNW were merged  
18 in one single data base because samples are all of inland origin and the list of elements analysed is identical. For  
19 the organic micropollutants, the data of FNN, WNN and WNNW were grouped together, whereas the FSCMN  
20 data bas was analysed separately because it includes a list of substances (see [Table 1 of Electronic  
21 Supplementary Material](#)) far more extensive than the other data bases. The two data bases with sediments from  
22 marine origin were merged to increase the number of samples considered in the statistical analysis.  
23

24 All data refer to the sediment fraction <2 mm. The procedures used for extractions and analyses by the various  
25 networks are international ISO (e.g., 11885, ISO 2009; 15586, ISO 2004), EPA (e. g. 3050 B, 3051, 3052; EPA  
26 2009 a to c) or AFNOR (e.g., X 33-012, AFNOR 2000; X 31-147, AFNOR 1996) standard procedures. It was  
27 not possible to collect information on quality control procedures applied by all the laboratories involved in the  
28 six different monitoring programs covering two countries. The resulting possible bias and errors were considered  
29 less important than the interest of addressing very large data bases with sediments of contrasted origins and  
30 contamination levels.  
31

32 The data treatment consisted in replacing all values < detection limit (DL) by half the value of DL (European  
33 Commission 2009 a; European Commission 2006; Farnham et al. 2002; Ministère Québécois du Développement  
34 durable de l'Environnement et des Parcs 2009). Other statistical methods can be preferred over such a simple  
35 approach (Helsel and Hirsch 1991) but they were not applied here since our work did not focus on the lowest  
36 values, but on the most frequent and highest ones. Indeed, it is mainly for the estimation of the low values of  
37 statistical distributions that the simple systematic substitution is likely to introduce a bias (Caudill et al. 2007).  
38 No bias is introduced for estimating the median values or the 95<sup>th</sup> percentile as long as the percentage of  
39 values < DL does not exceed 1/3 or 2/3 of the total population, respectively (Caudill et al. 2007). For the  
40 parameters considered here, the percentages of values < DL never reached levels likely to introduce a bias in the  
41 statistical examination of the high values, which are those of concern in the assessment of the hazardous  
42 character of the sediments. Finally, the comparison between several procedures for taking into account values <  
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DL shows that the replacement by DL/2 gives better results than the replacement by DL or zero (Farnham et al. 2002).

Descriptive statistical analyses were conducted with the XLSTAT 2008 4.01 software. Besides scattergram diagrams, linear correlations between pairs of trace elements were examined (Pearson correlation coefficient, and slope of the correlation) for the hazardous substances identified as possibly present in sediments and including two trace elements ( $ZnCrO_4$ ,  $PbHAsO_4$ ,  $PbCrO_4$ ; see 2.2.2). If the measured total trace elements concentrations correspond only (or mainly) to these dangerous substances, a hypothesis maximizing the potential hazard, the linear correlations between the concentrations (mg/kg) of pairs of trace elements should be highly significant (0.01 level) with a slope of the correlation (or median ratio of concentrations) equal (or very close) to the ratio of atomic mass of the two elements considered, i. e. 1.26 for the correlation Zn/Cr, 0.8 for Cr/Zn, 2.77 for Pb/As, 0.36 for As/Pb, 3.99 for Pb/Cr, and 0.25 for the correlation Cr/Pb. Such an indirect estimation of the possible presence of dangerous inorganic substances is made necessary by the fact that neither chemical techniques for operationally-defined speciation of metals (Tessier et al. 1979), nor more specific spectroscopic techniques (O'Day et al. 2000; Panfili et al. 2005; Peltier et al. 2005) enable the identification of specific substances.

## **2.2 Short update on the European Union legislative framework on wastes and sediment management**

The Directive 2008/98 (European Commission 2008 a) on waste repeals the previous EU directives. Dredged sediments are classified as waste; their management has to be in accordance with the Waste Hierarchy and depends on their content of dangerous substances. Recovery and valorisation of the materials could be one of the management options. Article 6 of Directive 2008/98 defines the end-of-waste status, applicable to sediments, which could therefore be bound by the Chemical Substances and Preparations regulation (EC) 1907/2006 (so called REACH) and will need to pass the test of H7, H10 and H11 criteria. In parallel, the 25-26 September 2008 meeting of the Competent Authorities for the implementation of REACH concluded "...As soon as a material 'ceases to be waste' in a recovery process, REACH requirements apply in principle as to any other material..." (European Commission, 2008 b). The same group provides updated definitions of "substances of Unknown or Variable composition, Complex reaction products or Biological material" and "articles" that fall under REACH legislation and clearly apply to sediments. Finally, the working group for the amendment of the European waste list (summary record of the meetings held on 5 and 6 November 2009, unpublished document 21/12/2009, GW/amp-env.g.2(2009)436598) is discussing the definition of H criteria to be applied to wastes, not only substances and preparations.

The application to sediments of the generic concentrations of H7, H10 and H11 related to the regulation of Classification, Labelling and Packaging of dangerous substances (European Commission 2008 c) is therefore in line with the up-to-date EU legislation.

## **2.3 Selection of the dangerous substances with CRM properties possibly present in sediments**

The list and classification of dangerous substances according to H7, H10 and H11 is updated annually by the European Commission; the version used in this work is dated of January 2009 (European Commission 2009 b). Linking this list with the threshold concentrations set for hazardous wastes leads for each substance to the threshold concentration above which the waste will be classified as hazardous. For the organic micropollutants,

1 the procedure is straightforward since the analyses available for sediments relate indeed to the substances  
2 themselves. By contrast, the hazard due to metals and metalloids can not be assessed directly since sediment  
3 monitoring programs provide data on total trace elements concentrations, not on the substance in which the  
4 element may be included. The first step of our work was therefore to identify for the trace elements analysed in  
5 the data sets available (As, Cd, Cr, Co, Cu, Hg, Ni, Pb, Zn) and included in dangerous substances (all elements  
6 but Cu and Hg that are not included in any of the dangerous substances from the EU list, European Commission  
7 2009 b), which dangerous substances were most likely to be present in sediments. This step was taken through a  
8 literature review on aqueous solubility and on metal speciation in sediments.  
9

### 10 11 12 13 *2.3.1 Literature review of aqueous solubility of the dangerous inorganic substances including trace elements* 14 *analysed in routine sediments monitoring programs* (Table 1)

15 For arsenic, the high aqueous solubility of arsenic oxides and arsenic acid, and the possible biodegradation of the  
16 ethyl groups of triethyl arsenate result in  $As_2O_5$ ,  $As_2O_3$ ,  $(C_2H_5O)_3AsO$  and  $H_3AsO_4$  being excluded of the  
17 substances to be considered in sediments. By contrast, pH-pe equilibrium modelling with data from river  
18 sediments shows  $HAsO_4^{2-}$  to be stable for  $pH > 6,8$  and redox potential  $> 130$  mV (Blute et al. 2009);  $PbHAsO_4$   
19 will therefore be selected as substance of relevance for arsenic (and lead).  
20

21 For Cd, the low aqueous solubility of sulphide and oxide leads to the two substances being considered as  
22 possibly present in sediments.  
23

24 For cobalt, the very low aqueous solubility of carbonate may lead to  $CoCO_3$  being present in sediments.

25 Chromate is a frequent constituent of CRM substances. However, calcium, potassium, sodium, strontium and  
26 ammonium chromates have such high a high aqueous solubility that their presence in sediments is very unlikely.  
27 The case of zinc and lead chromates is quite different; only slightly soluble in water, they can possibly be present  
28 in the solid fraction of sediments. Indeed, the presence of poorly soluble chromates in some sediments can not be  
29 ruled out (Lespagnol 2003; Barnhart 1997) and hexavalent chromium is naturally present in the mineral  $PbCrO_4$   
30 (Zayed and Terry 2003). Zinc and lead chromates will therefore be included for the evaluation of the CRM  
31 properties of sediments in link with the total chromium content.  
32

33 For nickel, the oxide, hydroxide and carbonate should be considered since their aqueous solubility is very low.  
34 Nickel trioxide is a very strong oxidant (INRS 2009) that would be reduced by the organic matter and sulphides  
35 (or other reduced species) of sediments; it will therefore not be considered further.  
36

37 For lead, in addition to  $PbHAsO_4$  and  $PbCrO_4$ ,  $Pb_2(PO_4)_3$  will be considered even though pure metal phosphate  
38 minerals are unlikely to form under the environmental conditions prevailing in most soils and sediments  
39 (Martinez et al. 2004). By contrast, the highly explosive and sensitive nature of lead azide makes its presence in  
40 sediment highly unlikely.  
41

42 For zinc, chromate is the only reported CRM substance and it will be taken into consideration since poorly  
43 soluble chromates can be present in some sediments (Lespagnol 2003; Barnhart 1997).  
44

### 45 46 47 48 49 50 51 52 53 54 *2.3.2 Literature review on the speciation in sediments of trace elements analysed in routine sediment monitoring* 55 *programs*

56 Most papers reviewed rely on the sequential extraction developed by Tessier (Tessier et al. 1979), modified to  
57 various degrees, mostly for As (e.g., Blute et al. 2009). A few papers report results from spectroscopic methods  
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(O'Day et al. 2000; Panfili et al. 2005; Peltier et al. 2005). The detailed outcome of the literature review is available as [Table 2 in the Electronic Supplementary Material](#); a summary is presented below.

*Arsenic* The most recent studies with the extraction procedure most adapted to As show the prevalence of the exchangeable (Bluet et al. 2009) or sulphide fraction (Jay et al. 2005). The other studies, which rely on a more standard Tessier's protocol, associate most of As to the operationally defined "oxides" or "residual fraction". However, since arsenic oxides have very high aqueous solubility (see Table 1), the fraction of As extracted from sediments using the reagents targeting the "oxide" fraction are unlikely to be  $As_2O_5$  or  $As_2O_3$ , substances of possible interest for CRM considerations. The other fractions from chemical extraction do not allow to exclude the possible contribution of lead arsenate to the total As content of sediments. Based on the information from Table 1 and from the speciation studies,  $PbHAsO_4$  is selected as the CRM substance to be considered for As.

*Cadmium* The speciation is highly variable according to the sediments studied. The maximum relative contributions are 77%, 47% and 42% for the organic matter fraction (Martin et al. 1996), the hydroxide/oxide fraction (Pardo et al. 1990) and the sulphide fraction (Loska and Wiechula 2002), respectively. Spectroscopic methods applied to highly contaminated estuarine sediments (244 and 764 mg/kg) indicate that all of the Cd is present as sulphides (O'Day et al. 2000). Combining the information from Table 1 with the speciation studies leads to the selection of CdS and CdO as the CRM substances considered for Cd.

*Cobalt* The possibility of cobalt to be associated with the carbonate phase of marine and freshwater sediments is indicated by various studies (Akçay et al. 2003; Baruah et al. 1996; Yuan et al. 2004).  $CoCO_3$  can therefore be considered as a relevant CRM substance for cobalt in sediments. It must be noted however that the relative contribution of the carbonate phase to the total Co content of sediments seems limited to 10%.

*Chromium* Two studies on coastal sediments (some highly contaminated, 1 050 mg/kg) indicate the fraction associated with Fe and Mn oxides as dominant (60%), with the "organic matter" fraction being also a significant contributor (Graham et al. 2009; Lam et al. 1997). Several studies of lake sediments also indicate a significant contribution of the oxide (20–36%) and organic matter (10–40%) phases (Akçay et al. 2003; Fytianos and Lourantou 2004). Spectroscopic methods applied to an anoxic estuarine sediment shows chromium to be exclusively bound to oxygen atoms (O'Day et al. 2000). All the results from the reviewed speciation studies support the initial choice, based on aqueous solubility (see Table 1), of  $ZnCrO_4$  and  $PbCrO_4$  as the chromate-based CRM substances most relevant for the purpose of the present study.

*Nickel* Based on the chemical extraction results  $NiCO_3$  can be considered as a CRM substance possibly present in sediments, carbonates contributing to 16% (Pardo et al. 1990) or 34% (Lam et al. 1997) of the total Ni. The speciation studies do not provide information that would remove nickel hydroxide, monoxide and trioxide from the list of CRM substances possibly present in sediments. Four CRM substances holding Ni will therefore have to be considered.

*Lead* In most lake sediments studied (Tokalioglu et al. 2000; Fytianos and Lourantou 2004), in saltmarshes (Mortimer and Rae 2000; Reboreda and Caçador 2007) and in contaminated marine sediments (Yuan et al. 2004), the organic/sulphide fraction is dominant. However, in a contaminated ( $Pb = 213$  to  $1269$  mg/kg) reduced estuarine sediment, spectroscopic methods indicate that Pb is bound to oxygen atoms, not to organic matter nor sulphides (O'Day et al. 2000). In canal and river sediments, the oxide and residual phases have been reported as the major constituents of the total lead content (Akçay et al. 2003; Baruah et al. 1996; Galvez-Cloutier and Dubé

1998; Savonina et al. 2006). The reported association of lead with oxide fraction or oxygen atoms confirm the choice made from Table 1 of  $\text{PbHAsO}_4$ ,  $\text{PbCrO}_4$  and  $\text{Pb}_3(\text{PO}_4)_2$  as CRM substances of interest.

*Zinc* According to the sediment studied, most of Zn is associated with the fraction operationally-defined as hydroxides/oxides (Akçay et al. 2003) or sulphides (Panfili et al. 2000; Tokalioglu et al. 2000; O'Day et al. 2000; Peltier et al. 2005) or residual (Isaure et al. 2001; Yuan et al. 2004). The contribution of  $\text{ZnCrO}_4$  to a fraction of Zn being present in the operational fraction "hydroxides/oxides" can not be totally excluded, and zinc chromate will be considered in the following data analysis.

## 2.4 Threshold values selected for the data analysis

For each inorganic CRM substance identified as possibly present in sediments, the threshold value associated to its classification into category 1, 2 or 3 of criterion C, M or R, has been transformed into the corresponding trace element total concentration (Table 2), based on the assumption that all of the trace element is present solely as the substance considered. For instance, the limit value in a non hazardous waste for zinc chromate,  $\text{ZnCrO}_4$ , being 1000 mg/kg (0.1%, carcinogenic category 1), the limit value for total zinc, considered present solely as  $\text{ZnCrO}_4$ , is 361 mg/kg (1000 mg/kg \* atomic mass of Zn/molecular weight of  $\text{ZnCrO}_4$ ). For Cd, Cr, Ni and Pb, more than one CRM substance was identified by the literature review; the most stringent threshold value (substance in bold type, see Table 2) will be considered. This overall procedure is clearly very conservative.

## 3 Results and discussion

### 3.1 Organic substances with CRM properties in the data set from the French Surveillance Control Monitoring Network (FSCMN)

This data set, covering all of French inland surface waters, is the most comprehensive one regarding the number of substances analysed (168; see Table 1 of the Electronic Supplementary Material) and the number of samples (up to 1630, depending on the substance).

The substances with CRM properties quantified in at least 0.5% of the data set consist of 6 polycyclic aromatic hydrocarbons (PAH), 1 phthalate, 1 aromatic hydrocarbon, 1 nonylphenol, 2 herbicides and 4 chlorinated aliphatics (Table 3). None of these are however classified as known CRM (category 1), seven are suspected CRM (category 2), and eight are classified as possible CRM (category 3).

The maximum concentration of CRM substances, 62 mg/kg for benzo(a)pyrene, remains 16 times lower than the threshold concentration above which the sediment would be classified as « hazardous ». Six other PAHs show maximum concentrations of the same order of magnitude. Toluene is one order of magnitude lower than benzo(a)pyrene and has a threshold value 50 times greater, so that the safety margin for toluene is a factor of 33 333. The maximum ethyl hexyl phthalate (EHP) concentration is of the same order of magnitude as for benzo(a)pyrene, but the threshold concentration for EHP is 5 times higher so that the maximum value is 278 times below the threshold. The maximum for 4 para-nonylphenol is of the same order as the PAHs, but its threshold value 50 times greater, so that the safety margin is a factor of 962. The maximum concentrations observed for herbicides and chlorinated aliphatics are between 100,000 and 1,000,000 times lower than the threshold value. Since the threshold value is not approached for any organic substance, the scattergrams of the concentrations are not presented.



### 3.2 Organic substances with CRM properties in the data set from the inland sediments of Northern, Eastern and Central French navigable waterways, and Walloon navigable and non-navigable waterways

The data from the Walloon non navigable waterways could not be merged with the other inland data sets because they are presented by groups of substances, not as individual substances. Indeed, the results for PAHs are expressed as the sum of the 16 PAHs from the EPA list, and the results of benzene and toluene are not available individually (the value reported is the sum of benzene, toluene, ethylbenzene and xylenes). As for chlorinated pesticides, the results are expressed as the sum of hexachlorobenzene (HCB; carcinogenic C2), aldrin (C3), dieldrine (C3), endrine, isodrine, lindane, heptachlor epoxide, 4,4 DDE, 2,4 DDT and 4,4 DDT. For the interpretation of the data from the Walloon non navigable waterways, the total concentration of each group of substances was assumed to be the concentration of the most dangerous CRM category of the group.

The maximum concentration is 35.9 mg/kg for chrysene (Table 4), a value 28 times lower than the threshold. The other 5 PAHs analysed, and toluene, show maximum concentrations of the same order of magnitude. Benzene and hexachlorobenzene are 2 orders of magnitude lower than the PAHs. None of these substances is therefore likely to pose a CRM hazard in the sediments sampled.

The concentrations of the chlorinated pesticides are similar to literature data, 0.003 mg/kg for atrazine (Holvoet et al. 2007) and 0.033 mg/kg for DDTs (Liu et al. 2008). Higher concentrations of chlorinated pesticides are reported in the literature, e.g., 0.45 mg/kg for lindane (Villaverde et al. 2008) and 0.81 mg/kg for the sum of 18 substances (Malik et al. 2009), but even these extreme values remain far below the threshold for these substances. Based on the threshold values set by the EU directive on wastes, the CRM hazards resulting from pesticides in inland sediments can therefore be disregarded.

### 3.3 Organic substances with CRM properties in the data set from the French marine sediments monitoring networks

Six PAHs are analysed in both RNO and REPOM networks, while the chlorinated pesticides are analysed only in the RNO network.

The maximum concentration of the CRM organic substances analysed (Table 5) is much lower (37 times, chrysene) than the threshold concentration. The two chlorinated pesticides pose even less problem, with a safety margin of a factor 27 778 for pp'-DDT and 833 333 for  $\alpha$ -HCH. The organic contaminants with CRM properties analysed in the French marine sediments do not get anywhere close to the threshold value that would lead to the classification of the sediments as hazardous wastes on the basis of the H7, H10 and H11 criteria.

### 3.4 Inorganic substances with CRM properties in the data set from the French marine sediments monitoring networks (RNO + REPOM)

Total trace element concentrations exceeding the threshold concentration are observed for Cr, Pb and Zn (Table 6). It must be recalled that the threshold concentration is the total trace element concentration that would lead to the classification of the sediment as hazardous waste if the total concentration resulted entirely from the substance with CRM properties identified as possibly present in sediments.

The statistical distributions of Cr, Pb and Zn concentrations illustrated by scattergrams in Fig. 1 shows that the proportion of samples exceeding the threshold is greatest for Zn (9%), less for Cr (1.2%), and lowest for Pb (0.07%).

1 The interpretation of the data will consider the uncertainty associated with the extraction and analysis  
2 procedures. The precision of trace elements concentrations determined in reference materials varies according to  
3 the element, and, for each element, generally decreases with increasing concentrations (Table 7). The reported  
4 reproducibility will be used in the data treatment to ensure that only the samples with concentrations exceeding  
5 the threshold concentration by more than the expected average variability will be considered as really posing a  
6 possible CRM hazard.

7  
8 For the samples with Cr concentrations greater than the threshold of 161 mg/kg, the hypothesis of Cr being  
9 present mainly as Pb or Zn chromate was checked by looking at the correlations between Cr and Zn, and Cr and  
10 Pb concentrations. The linear correlations are not statistically significant at the 5% level (data not shown). For Cr  
11 and Pb, the ratio between Cr and Pb concentrations that would result from all Cr being present as  $\text{PbCrO}_4$ , 0.25,  
12 is not observed for any sample. Actually, the mean ratio between Cr and Pb concentrations for the 14 samples  
13 with  $\text{Cr} > 161$  mg/kg is 12.3, the median is 7.5, and no sample shows a ratio within 50% of the threshold ratio  
14 (50% is taken here as an estimate of the cumulated uncertainties linked to the use of ratios of concentrations).  
15 For Cr and Zn, the theoretical ratio between concentrations that would result from all Cr being present as  
16  $\text{ZnCrO}_4$  is 0.17; the mean ratio observed for the 14 samples with  $\text{Cr} > 161$  mg/kg is 3.4, the median is 1.6, and  
17 the only sample with a ratio, 0.19, within 50% of the theoretical value has a total Cr concentration of 163 mg/kg  
18 which falls in the 12% uncertainty for Cr determinations in that range of concentrations in sediments (see Table  
19 7). These observations strongly, albeit indirectly, suggest that in the marine sediments where Cr exceeds the  
20 threshold, Cr is not present as lead or zinc chromate. The hazard due to Cr present as  $\text{PbCrO}_4$  or  $\text{ZnCrO}_4$  can  
21 therefore be disregarded.

22 The same type of data analysis must also be conducted for the samples that exceed Zn or Pb thresholds.

23 For Pb, only one sample exceeds 597 mg/kg. Its corresponding Cr concentration, 391 mg/kg, yields a Pb/Cr  
24 mass ratio of 1.5 that does not satisfy the hypothesis of Pb being fully present as  $\text{PbCrO}_4$  (the Pb/Cr mass ratio in  
25  $\text{PbCrO}_4$  is 3.99). For the sample with  $\text{Pb} > 597$  mg/kg, the corresponding As concentration, 32 mg/kg, yields a  
26 Pb/As mass ratio of 18.7 that does not, by far, satisfy the hypothesis of Pb being entirely present as  $\text{PbHAsO}_4$   
27 (the Pb/As mass ratio in  $\text{PbHAsO}_4$  is 2.77). In this outlier sample, Pb is therefore not present as  $\text{PbCrO}_4$  nor  
28  $\text{PbHAsO}_4$  and no CRM hazard linked to Pb can be attributed to the sample.

29 For the 120 samples where Zn exceeds the threshold, the hypothesis of Zn being present as  $\text{ZnCrO}_4$  requires the  
30 ratio of Zn to Cr concentrations to be 1.26. Now, the linear correlation between  $\text{Zn} > 395$  and Cr is not  
31 statistically significant at the 5% level (data not shown), and the mean ratio of Zn/Cr concentrations in samples  
32 with  $\text{Zn} > 361$  mg/kg is 14, the median being 8.2. The only sample showing a ratio Zn/Cr, 1.2, within 50% of the  
33 theoretical value; has a total Zn concentration of 406 mg/kg, hardly greater than the Zn threshold value of  
34 395 mg/kg. The 14% uncertainty on Zn determinations in sediments for this range of concentrations (see Table  
35 7) means that the actual concentration may well be in fact lower than the threshold value. Therefore, it is not  
36 quite sure that this given sample satisfies the criteria leading to its classification as possibly hazardous on the  
37 basis of carcinogen property category 1 linked to  $\text{ZnCrO}_4$ .

### 3.5 Inorganic substances with CRM properties in the data set from the French and Walloon inland sediments monitoring programs

To various degrees, the threshold value of the CRM substance considered is exceeded for all the trace elements (Table 8). The greatest relative exceedance ( $R = \text{maximum value}/\text{threshold value}$ ) is observed for Zn, with  $R = 395$ ; the smallest relative exceedances are observed for As, Co, Cr and Ni, with  $R = 4.7$  to  $5.0$ . The proportion of values exceeding the threshold ranges from 0.1–0.2% for As, Cd and Ni, to 27% for Zn. The detailed distribution of values is illustrated in Fig. 2.

For Cd, Co and Ni, the analytical data available do not enable to assess if the rare exceedances are actually due to the presence of the CRM substance on which the threshold value is based. An indirect reasoning based on the literature review on metal speciation in sediments will therefore be applied. The maximum relative exceedance observed for Co is equal to 5, whereas a value of 10 would be needed to suggest a CRM hazard due to  $\text{CoCO}_3$  since the maximum contribution of the carbonate fraction reported in speciation studies of Co in sediments is 10% (Akçay et al. 2003). By contrast, the maximum relative exceedances observed for Cd and Ni (9 and 5, respectively) may actually correspond to a CRM hazard since  $\text{CdS}$  and  $\text{NiCO}_3$ , the CRM substance considered to set the threshold, may represent 100% of the total Cd (O'Day et al. 2000) and 16–34% of the total Ni (Lam et al. 1997; Pardo et al. 1990) concentration in the sediment. For Ni, considering 34 or 16% as the possible contribution of  $\text{NiCO}_3$  to the total Ni concentration, only 3 or 0 samples would constitute a possible CRM hazard resulting from  $\text{NiCO}_3$ . For Cd, the 8 samples exceeding the threshold value may constitute a CRM hazard resulting from the substance  $\text{CdS}$  as defined by the legislation on wastes. The actual bioavailability of  $\text{CdS}$  and  $\text{NiCO}_3$  in sediments is however most likely to be much lower than the pure substances for which the CRM hazards have been assessed. Furthermore, once sediments are exposed to aerobic conditions such as during resuspension or ripening on land, metal sulphides are known to be prone to oxidation which may result in the progressive disappearance of substances such as  $\text{CdS}$  (Chapman et al. 1998, di Toro et al. 1992, du Laing et al. 2007, O'Day et al. 1998). Sediment acidification resulting from oxidation of organic matter and sulphides (Petersen et al. 1997) may also lead to transformation of carbonate forms such as  $\text{NiCO}_3$ . The real CRM hazard posed by the possible presence of  $\text{CdS}$  (8 samples, 0.2% of the total number of samples) and  $\text{NiCO}_3$  (3 samples, 0.08% of the total number of samples) in sediments that would be managed as wastes is therefore very likely to be negligible.

For As, Cr, Pb and Zn, the analysis of the correlations between pairs of elements can give an insight into the possibility that the CRM substances considered for each of these 4 trace elements represent actually a significant part of the total metal concentrations.

#### 3.4.1 Cr in $\text{ZnCrO}_4$

For the 98 samples where  $\text{Cr} > 161 \text{ mg/kg}$ , the slope of the linear correlation (significant at the 0.1% level) between Cr and Zn concentrations is 0.03 (Fig. 3) and the median ratio between Cr and Zn concentrations is 0.2, whereas the two parameters should equal 0.8 if all the total Cr was present as  $\text{ZnCrO}_4$ . However, seventeen samples show a ratio Cr/Zn within 50% of the theoretical value, and twelve of them have a Cr concentration greater than the Cr threshold + 15% (15% is taken here as common analytical uncertainty on Cr determinations in sediments, see Table 7). These 12 samples (0.4% of the total number of samples) may be considered as posing a possible hazard due to the presence of Cr as  $\text{ZnCrO}_4$ .

#### 3.4.2 Zn in $\text{ZnCrO}_4$

1 For the 877 samples where  $Zn > 361$  mg/kg, the slope of the linear correlation (significant at the 0.1% level)  
2 between Zn and Cr concentrations is 4 (Fig. 4) and the median ratio between Zn and Cr concentrations is 12,  
3 whereas a value of 1.3 is expected for samples in which all Zn would be present as  $ZnCrO_4$ . Only 4 samples are  
4 within 50% of the theoretical ratio of 1.3, and only 3 of these 4 have Zn concentrations exceeding the threshold  
5 total Zn concentration by 20% or more. The possible CRM hazard linked to  $ZnCrO_4$  is therefore limited to 0.09%  
6 of the 3,412 sediment samples analysed.  
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#### 10 3.4.3 Pb in $PbCrO_4$

11 For the 80 samples where  $Pb > 597$  mg/kg, the slope of the linear correlation (significant at the 0.1% level)  
12 between Pb and Cr concentrations is  $-2.1$  (Fig. 5) and the median ratio between Pb and Cr concentrations is 13,  
13 whereas it would be 4 for a sample with all Pb present as  $PbCrO_4$ . Four samples exhibit a Pb/Cr ratio within 50%  
14 of the theoretical value, but none exceeds the threshold concentration of Pb by at least 20%. In the samples  
15 exceeding the total Pb concentration that would lead to the sediment being classified as hazardous on the basis of  
16 possible carcinogenic effect of  $PbCrO_4$ , Pb is actually not present mainly as  $PbCrO_4$  and no CRM hazard  
17 resulting from lead chromate can be attributed to these samples.  
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#### 24 3.4.4 Cr in $PbCrO_4$

25 For the 98 samples where  $Cr > 161$  mg/kg, the slope of the linear correlation (significant at the 0.1% level)  
26 between Cr and Pb concentrations is 0.18 (Fig. 6) and the median ratio between Cr and Pb concentrations is 1.2,  
27 whereas it would theoretically be 0.25 for a sample with all Cr present as  $PbCrO_4$ . However, thirteen samples  
28 exhibit a Cr/Pb ratio (0.14, 0.21, 0.22, 0.26, 0.28, 0.29, 0.32, 0.33, 0.34, 0.37, 0.37, 0.38, 0.40) within 50% of the  
29 theoretical value, nine of which also exceeds the threshold total Cr concentration by 20% or more. Some  
30 potential CRM hazard can therefore be associated with Cr in these 9 samples, representing 0.3% of the total  
31 number of sediments for which Cr data are available.  
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#### 38 3.4.5 Pb in $PbHAsO_4$

39 For the 80 samples where  $Pb > 597$  mg/kg, the slope of the linear correlation ratio (significant at the 0.1% level)  
40 between As and Pb concentrations is 91 (Fig. 7) and the median ratio between Pb and As concentrations is 55,  
41 whereas it would be 2.8 for a sample with all Pb present as  $PbHAsO_4$ . No sample exhibits a Pb/As value within  
42 50% of 2.8. A possible CRM hazard resulting from all the total Pb being present as  $PbHAsO_4$  can therefore be  
43 ruled out in all of the 3 448 sediment samples where As and Pb concentrations were analysed in the same  
44 sample.  
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#### 50 3.4.5 As in $PbHAsO_4$

51 For the 3 samples where  $As > 216$  mg/kg, the ratios between As and Pb concentrations are 0.01, 0.02 and 4.7,  
52 whereas it would be 0.4 for a sample with all As present as  $PbHAsO_4$ . No CRM hazard due to the hypothesis of  
53 As being present as  $PbHAsO_4$  should therefore be considered.  
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## 57 4 Conclusions

1 The objectives of this paper were twofold: firstly, to develop a methodology for applying the H7, H10 & H11  
2 criteria to sediments for their management if dredged and, secondly, to see what the application of the  
3 methodology can tell about sediments in the chosen data sets.

4 The methodology developed is applicable to results from routine sediment monitoring programs and takes into  
5 consideration the latest (known as of March 2011) development of the EU legislation related to sediment  
6 management. It relies on the data that are the most commonly available in analytical programs conducted  
7 routinely on hundreds of samples (just in France) yearly. More sophisticated techniques (e.g. X-Ray Diffraction,  
8 X-ray Absorption Spectroscopy, Extended X-ray Absorption Fine Structure) can provide detailed information on  
9 metal speciation in/on solid phases (O'Day et al. 2000, Isaure et al. 2001, Panfili et al. 2005, Peltier et al. 2005,) but they have two major shortcomings. First, they apply to minute amounts of sediments ( $\mu\text{m}^3$  to  $\text{mm}^3$ ,  
10 depending on the equipment used), raising the issue of representativeness of the observations made. Second, they  
11 are not standardized or available in a sufficient number of laboratories to be used on a large number of samples.  
12 As things stand, the use of such techniques can only be promoted, not recommended, even less so prescribed.

13 The data bases examined contain samples that exceed the maximum trace element concentrations reported  
14 recently in the literature for sediments from different mining and smelting areas (Aleksander-Kwaterczak and  
15 Helios-Rybicka 2009). For organic micropollutants, the concentrations in this study are also extremely high,  
16 exceeding for instance the values set by the Norwegian environmental quality classification for "very bad  
17 quality" sediments (Bakke et al. 2010). It can therefore be assumed that the data examined here include "worst  
18 case" sediments as far as commonly analysed total trace elements and organic micropollutants are concerned.

19 Despite these worst case samples, the CRM hazard ("CRM hazard" should be understood as in the sense of the  
20 EU Waste Directive) posed by trace elements is negligible, both as regards the number of samples potentially  
21 affected (maximum observed: 9 samples out of 3,443 for Cr) and as regards the real CRM hazard linked to the  
22 management of dredged sediments as wastes. Indeed, for trace elements, the dangerous inorganic substances  
23 possibly present in sediments relate to chromate, sulphide and carbonate species that are strongly bound to  
24 sediments. The corresponding CRM hazard would therefore be far lower than for readily bioavailable species,  
25 such as the pure substance in an aqueous matrix for instance. Furthermore, the evolution of metal speciation  
26 during the land disposal of sediments in oxic conditions notably involves a decrease in the sulphide and  
27 carbonate forms which are, according to the EU list of dangerous substances and the likely presence of those  
28 substances in sediments, the possible source of a CRM hazard for Cd, Co and Ni.

29 For organic micropollutants, the list of dangerous substances determining the hazardous character of a waste is  
30 far more extensive and includes substances of greater CRM hazard than the list of substances analysed in routine  
31 sediment monitoring networks. Now, the threshold value for the most exacting CRM category, C1, is in fact the  
32 same as that of C2 or M2 categories, which correspond to substances analysed in sediment monitoring networks.  
33 The maximum concentration in the data sets examined, even considering substances with no CRM properties  
34 and the extensive list of 168 substances analysed in the FSCMN, was 101 mg/kg for both pyrene and  
35 fluoranthene, well below the threshold value of a C1 substance. It therefore seems possible to disregard the CRM  
36 hazard posed by organic micropollutants in sediments, except for very specific and rare cases where sediments  
37 would receive a major input of a persistent dangerous organic substance with CRM properties of category 1. Our  
38 study does not however imply that the sediments analysed may not cause aquatic risks to species or communities  
39 living in or in contact with these sediments. The list of analytes included in the data bases does not indeed  
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1 include a series of organic substances found in sediments and causing adverse environmental effects, synthetic  
2 musks for instance (Peck et al. 2006; Gooding et al. 2006), dioxins, or perfluorinated and polybrominated  
3 compounds. However, the bioactive compounds in sediments cannot always be detected by traditional  
4 instrumental analyses (Mazurová et al. 2010) and they are not all included in the list of dangerous substances on  
5 the basis of which the hazardous character of wastes is determined. Integrated assessment of contaminated  
6 sediments is required to elucidate their ecotoxicological impact (Mazurová et al. 2010), but the implementation  
7 of legislation such as the EU Waste Directive must also rely on existing knowledge and data bases, areas in  
8 which it is hoped that the present study will prove useful.

9 Taking into account the H7, H10 and H11 criteria in the assessment of the possible hazard caused by sediments  
10 in the RSMNs considered will not influence the possible management options of 99.4% of these sediments if  
11 they were dredged and disposed of on land.

12 Other criteria need however to be considered, notably criterion H14. Indeed, biotests of sediments often indicate  
13 ecotoxicity effects (Eklund et al. 2010; Jungmann et al. 2009; Wölz et al. 2009). The problem of criterion H14 is  
14 the lack of threshold values in the legislation and the lack of standardised batteries of biotests (Kosmehl et al.  
15 2007; Pane et al. 2008; Stevesic et al. 2007). Work is in progress to assess the H14 criterion for dredged  
16 sediments with a perspective of legislation, notably in France. The outcome of such work will enable a more  
17 thorough examination of the hazardous character of dredged sediments and lead to the identification of the most  
18 appropriate risk-based management options (Apitz 2008 a and b).

19 **Acknowledgements** The author thanks A. Morin (INERIS), C. Perard-Albin (VNF), Y. Libert (SPW, Belgium),  
20 D. de Thysebaert and J. L. Berger (DCE, Belgium), A. Huguet (IFREMER) and D. Claisse (IFREMER) for  
21 providing the data used in the present study. The help of I. Ignatiadis and S. Betelu (Brgm) in compiling the data  
22 on aqueous solubility was greatly appreciated. We would like to extend particular thanks, both professional and  
23 personal, to D. Darmendrail (BRGM), who proved most helpful in providing a clear, up-to-date view of the EU  
24 legislation and regulations on waste and sediment management.

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**Table 1** Aqueous solubility of the dangerous inorganic substances including the trace elements most commonly analysed in routine sediment monitoring programs

Trace element	CRM Substance	Solubility (g/100 g H <sub>2</sub> O)	Ref.	Trace element	CRM Substance	Solubility (g/100 g H <sub>2</sub> O)	Ref.	
<b>As</b>	PbHAsO <sub>4</sub>	insoluble	1	<b>Ni</b>	NiCO <sub>3</sub>	0.0043 (20° C)	1	
	As <sub>2</sub> O <sub>5</sub>	65.82 (20°C)	1		NiSO <sub>4</sub>	40.4 (25° C)	1	
	As <sub>2</sub> O <sub>3</sub>	2.05 (25°C)	1		NiCl <sub>2</sub>	67.5 (25° C)	1	
	(C <sub>2</sub> H <sub>5</sub> O) <sub>3</sub> AsO	n. a.			Ni(OH) <sub>2</sub>	0.00015 (20°C)	1	
	H <sub>3</sub> AsO <sub>4</sub>	16.7	2		Ni(NO <sub>3</sub> ) <sub>2</sub>	99 (25 °C)	3	
<b>Cd</b>	CdCl <sub>2</sub>	120 (25°C)	1		NiO	insoluble	1	
	CdCl <sub>2</sub> .5/2 H <sub>2</sub> O	121 (25°C)	1		Ni(O) <sub>2</sub>	decomposes	4	
	CdF <sub>2</sub>	4.36 (25° C)	1		Ni <sub>2</sub> O <sub>3</sub>	insoluble	1	
	CdSO <sub>4</sub>	76.7 (25° C)	1		NiS	insoluble	1	
	CdSO <sub>4</sub> . 8H <sub>2</sub> O	76.7 (25° C)	1		Ni <sub>3</sub> S <sub>2</sub>	n. a.		
	CdS	insoluble	1		Ni(CO) <sub>4</sub>	n. a.		
	CdO	insoluble	1		<b>Pb</b>	PbHAsO <sub>4</sub>	insoluble	1
<b>Co</b>	CoCO <sub>3</sub>	0.00014 (20°C)	1			PbCrO <sub>4</sub>	0.0000172 (20°C)	1
	CoCl <sub>2</sub>	56.2 (25°C)	1	Pb(N <sub>3</sub> ) <sub>2</sub>		0.023 (18°C)	1	
	Co(NO <sub>3</sub> ) <sub>2</sub>	103 (25°C)	1	Pb(CH <sub>3</sub> COO) <sub>2</sub>		44.3 (20°C)	1	
	CoSO <sub>4</sub>	38.3 (25°C)	1	Pb(C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> ) <sub>2</sub> 3H <sub>2</sub> O		very soluble	1	
	Co(CH <sub>3</sub> COO) <sub>2</sub>	very soluble	1	F <sub>6</sub> PbSi		n. a.		
<b>Cr</b>	CrO <sub>3</sub>	169 (25°C)	1	Pb <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>		insoluble	1	
	CaCrO <sub>4</sub> 2H <sub>2</sub> O	13.22 (20°C)	1	<b>Zn</b>	ZnCrO <sub>4</sub>	3.08	1	
	Cr <sub>2</sub> (CrO <sub>4</sub> ) <sub>3</sub>	n. a.			<b>Cr</b>	K <sub>2</sub> CrO <sub>4</sub>	65.025	1
	CrO <sub>2</sub> Cl <sub>2</sub>	n. a.				K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>	15.1 (25°C)	1
	PbCrO <sub>4</sub>	0.0000172 (20°C)	1			Na <sub>2</sub> CrO <sub>4</sub>	87.65 (25°C)	1
			SrCrO <sub>4</sub>			very soluble	1	
			ZnCrO <sub>4</sub>			3.08	1	
			(NH <sub>4</sub> ) <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>			37 (25°C)	1	

ref 1: Lide 2005

2: Wikipedia 2009

3: INERIS 2006

4: INERIS 2009

n. a.: not available

**Table 2** Inorganic CRM substances considered possibly present in sediments and including one (or two) trace element(s) analysed in routine sediment monitoring programs, and threshold concentration (total trace element concentration) that would lead to a classification as “hazardous waste” of a sediment in which the trace element would be present solely as the substance considered. The substances in bold type are the most stringent ones, considered in the rest of the data analysis

<b>Trace element</b>	<b>CRM substance(s) (CRM ranking)</b>	<b>Threshold concentration of trace element (mg/kg dry weight, &lt; 2 mm)</b>
<b>As</b>	<b>PbHAsO<sub>4</sub></b> (C1 R1 R3)	<b>216</b>
<b>Cd</b>	<b>CdS</b> (C2 M3 R3)	<b>778</b>
	CdO (C2 M3 R3)	875
<b>Co</b>	<b>CoCO<sub>3</sub></b> (C2 M3 R2)	<b>495</b>
<b>Cr</b>	<b>PbCrO<sub>4</sub></b> (C2 R1 R3)	<b>161</b>
	ZnCrO <sub>4</sub> (C1)	287
<b>Ni</b>	<b>NiCO<sub>3</sub></b> (C1 M3 R2)	<b>494</b>
	NiS (C1)	647
	NiO (C1)	787
	Ni(OH) <sub>2</sub> (C3)	6 330
<b>Pb</b>	<b>PbHAsO<sub>4</sub></b> (C1 R1 R3)	<b>597</b>
	PbCrO <sub>4</sub> (C2 R1 R3)	641
	Pb <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> (R1 R3)	3 831
<b>Zn</b>	<b>ZnCrO<sub>4</sub></b> (C1)	<b>361</b>

**Table 3** Descriptive statistics of the CRM organic substances quantified in at least 0.5% of the data set from the 2007 campaign of the French Surveillance Control Monitoring Network of sediments

SUBSTANCE	Number of samples	> Q L %	Max (mg/kg)	Median (mg/kg)	CRM category	Threshold conc. (mg/kg)
Benzo(a)anthracene	1323	76.1	58	0.003	C2	≥ 1 000
Chrysene	1323	67.3	49	0.078	C2 M3	≥ 1 000
Benzo(a)pyrene	1627	64.0	62	0.005	C2 M2	≥ 1 000
Benzo(k)fluoranthene	1630	63.4	27	0.022	C2	≥ 1 000
Ethyl hexyl phthalate	1526	49.5	18	0.050	R2	≥ 5 000
Dibenzo(ah)anthracene	1353	42.1	15	0.010	C2	≥ 1 000
Toluene	559	38.2	1.5	0.010	R3	≥ 50 000
Naphtalene	1630	21.1	9	0.010	C3	≥ 10 000
Diuron	924	4.9	0.070	0.001	C3	≥ 10 000
Nonylphenols	1362	2.7	53	0.010	R3	≥ 50 000
Isoproturon	924	1.6	0.025	0.001	C3	≥ 10 000
Trichloroethylene	380	0.8	0.014	0.003	C2 M3	≥ 1 000
Tetrachloroethene	778	0.8	0.013	0.001	C3	≥ 10 000
Chloroform	778	0.5	0.010	0.001	C3	≥ 10 000
Dichloromethane	778	0.5	0.133	0.001	C3	≥ 10 000

Q L: quantification limit

**Table 4** Descriptive statistics of the CRM organic substances analysed in the inland waterways of Northern, Central and Eastern France, and Wallony. Data from the Walloon non-navigable waterways are presented in italics

SUBSTANCE	Number of samples	Max (mg/kg)	Median (mg/kg)	CRM category	Threshold conc. (mg/kg)
Benzo(a)anthracene	1 128	30.3	0.4	C2	≥ 1 000
Benzo(a)pyrene	1 145	29.1	0.5	C2 M2	≥ 1 000
Benzo(k)fluoranthene	1 144	12.5	0.1	C2	≥ 1 000
Chrysene	1 128	35.9	0.6	C2 M3	≥ 1 000
Dibenzo(ah)anthracene	1 128	9.7	0.1	C2	≥ 1 000
Naphtalene	1 128	21.3	0.1	C3	≥ 10 000
<i>Σ 16 PAH (EPA list)</i>	<i>191</i>	<i>145</i>	<i>4.4</i>	<i>C2</i>	<i>≥ 1 000</i>
Benzene	568	0.4	0.001	C1 M2	≥ 1 000
Toluene	568	18.5	0.001	R3	≥ 50 000
<i>Σ BTEX</i>	<i>238</i>	<i>15.7</i>	<i>0.9</i>	<i>C1 M2</i>	<i>≥ 1 000</i>
Hexachlorobenzene	39	0.37	0.01	C2	≥ 1 000
α-HCH	30	0.04	0.01	C3	≥ 10 000
pp'-DDT	31	0.05	0.01	C3	≥ 10 000
<i>Σ chlorinated pesticides</i>	<i>238</i>	<i>&lt; 0.01</i>	<i>&lt; 0.01</i>	<i>C2</i>	<i>≥ 1 000</i>

**Table 5** Descriptive statistics for the CRM organic substances analysed in the French marine sediments routine monitoring networks

SUBSTANCE	Number of samples	Max. (mg/kg)	Median (mg/kg)	CRM category	Threshold conc. (mg/kg)
Benzo(a)anthracene	702	19.5	0.05	C2	≥ 1 000
Benzo(a)pyrene	952	22.4	0.05	C2 M2	≥ 1 000
Benzo(k)fluoranthene	879	10.6	0.04	C2	≥ 1 000
Dibenzo(ah)anthracene	448	0.6	0.003	C2	≥ 1 000
Chrysene	695	26.7	0.05	C2 M3	≥ 1 000
Naphtalene	656	5.0	0.02	C3	≥ 10 000
pp'-DDT	479	0.36	0.0001	C3	≥ 10 000
α-HCH	479	0.012	0.00005	C3	≥ 10 000



**Table 6** Descriptive statistics for the trace elements total concentrations of the data set from the French marine sediments monitoring networks

<b>Trace element</b>	<b>Number of samples</b>	<b>Max. (mg/kg)</b>	<b>Median (mg/kg)</b>	<b>Threshold conc. (mg/kg)</b>	<b>Substance considered CRM category</b>
<b>As</b>	800	69	13	≥ 216	<b>PbHAsO<sub>4</sub></b> ; C1
<b>Cd</b>	1 362	8.6	0.2	≥ 778	<b>CdS</b> ; C2
<b>Cr</b>	1 203	636	45	≥ 161	<b>PbCrO<sub>4</sub></b> ; C1
<b>Ni</b>	1 192	237	18	≥ 494	<b>NiCO<sub>3</sub></b> ; C1
<b>Pb</b>	1 361	662	33	≥ 597	<b>PbHAsO<sub>4</sub></b> ; C1
<b>Zn</b>	1 360	2 800	105	≥ 361	<b>ZnCrO<sub>4</sub></b> ; C1

**Table 7** Examples of analytical uncertainty in trace metal determinations in sediments or sewage soil amended soil

<i>Ref. and matrix / Parameter</i>	Trace element			
	As	Cr	Pb	Zn
<i>ISO 15586; sediment</i>				
Concentration (mg/kg)	16.3	51	n. a.	n. a.
Reproducibility (C. V.,%)	26.2	21.7	-	-
<i>Bettinelli et al. 2000; CRM 277 estuarine sediment</i>				
Concentration (mg/kg)	n. a.	192	146	547
Reproducibility (C. V.,%)	-	12	22	14
<i>Bettinelli et al. 2000; CRM 143 sewage sludge amended soil</i>				
Concentration (mg/kg)	n. a.	188	1173	1155
Reproducibility (C. V.,%)	-	6	10	9

n. a. : not analysed

**Table 8** Descriptive statistics for the trace elements total concentrations of the data set from the French and Walloon inland sediments monitoring networks

Trace element	Number of samples	Max. (mg/kg)	Median (mg/kg)	Threshold conc. (mg/kg)	Substance considered CRM category
<b>As</b>	3 348	1 005	6.7	≥ 216	<b>PbHAsO<sub>4</sub></b> ; C1
<b>Cd</b>	4 012	7 285	0.8	≥ 778	<b>CdS</b> ; C2
<b>Co</b>	1 104	2 490	10	≥ 495	<b>CoCO<sub>3</sub></b> ; C2
<b>Cr</b>	3 443	750	37	≥ 161	<b>PbCrO<sub>4</sub></b> ; C1
<b>Ni</b>	3 994	2 380	19.2	≥ 494	<b>NiCO<sub>3</sub></b> ; C1
<b>Pb</b>	3 996	50 420	34	≥ 597	<b>PbHAsO<sub>4</sub></b> ; C1
<b>Zn</b>	3 412	142 500	148	≥ 361	<b>ZnCrO<sub>4</sub></b> ; C1

## Figure captions

**Fig 1** Scattergram of Cr, Pb and Zn concentrations from the French marine sediments monitoring networks. The full line around the centre of the distribution is the median, while the dashed line corresponds to the threshold concentration

**Fig 2** Scattergram of As, Cd, Co, Cr, Ni, Pb and Zn concentrations in the sediments from the French and Walloon inland monitoring networks. The full line around the centre of the distribution is the median, while the dashed line corresponds to the threshold concentration. The white cross is the mean value

**Fig 3** Linear correlation between samples with Cr > 161 mg/kg and the Zn concentrations in the corresponding samples from the French and Walloon inland monitoring networks

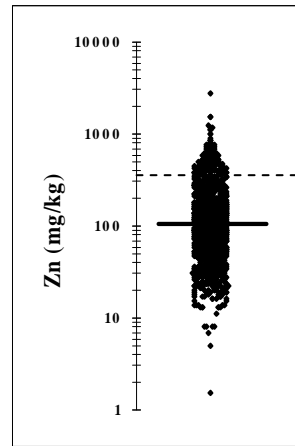
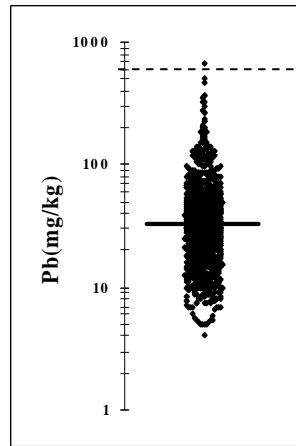
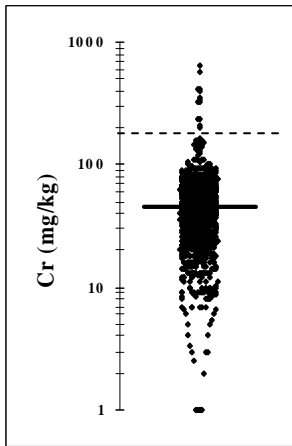
**Fig 4** Linear correlation between samples with Zn > 361 mg/kg and Cr concentrations in the corresponding sediments samples from the French and Walloon inland monitoring networks

**Fig 5** Linear correlation between samples with Pb > 597 mg/kg and the Cr concentrations in the corresponding sediment samples from the French and Walloon inland monitoring networks

**Fig 6** Linear correlation between samples with Cr > 161 mg/kg and the Pb concentrations in the corresponding sediment samples from the French and Walloon inland monitoring networks

**Fig 7** Linear correlation between samples with Pb > 597 mg/kg and the As concentrations in the corresponding sediment samples from the French and Walloon inland monitoring networks

Figure 1



**Figure 2**

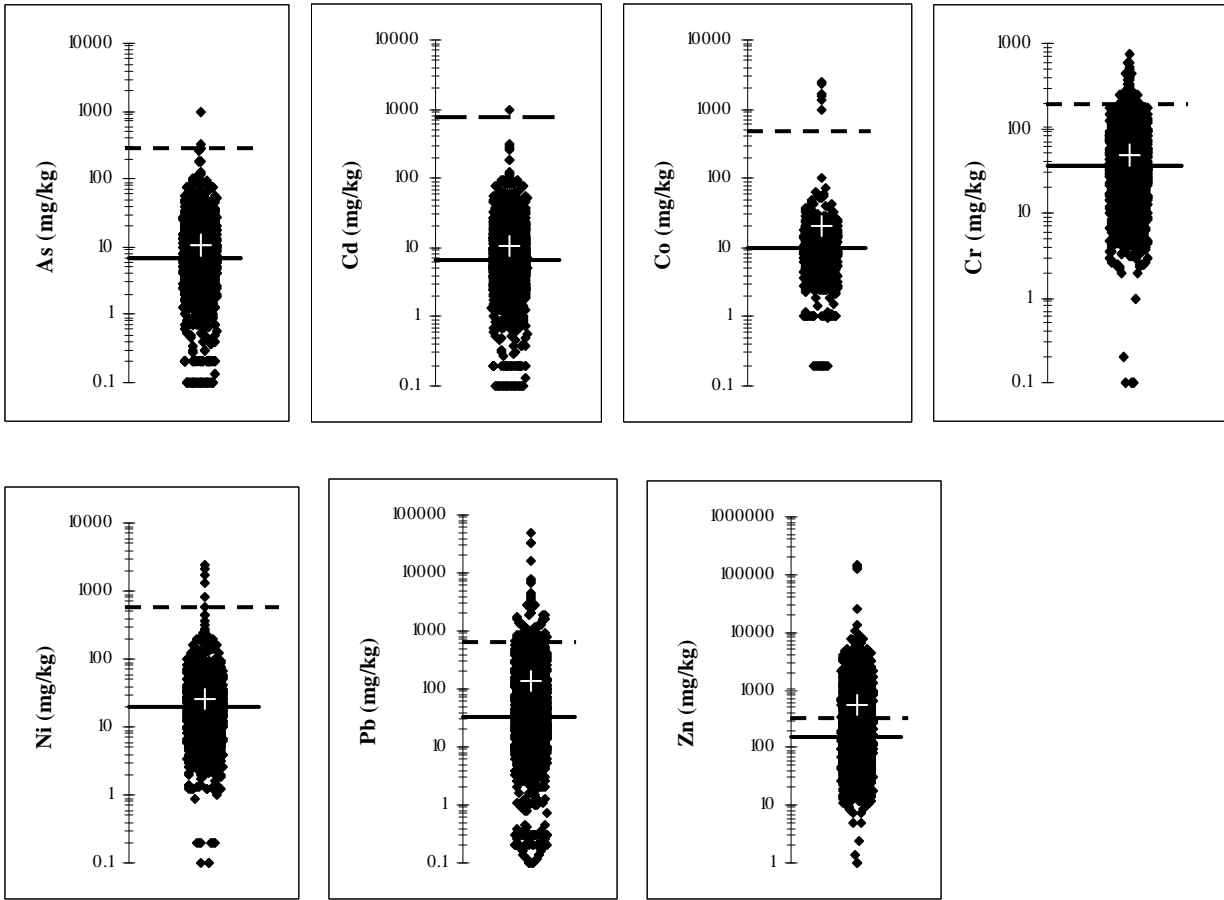
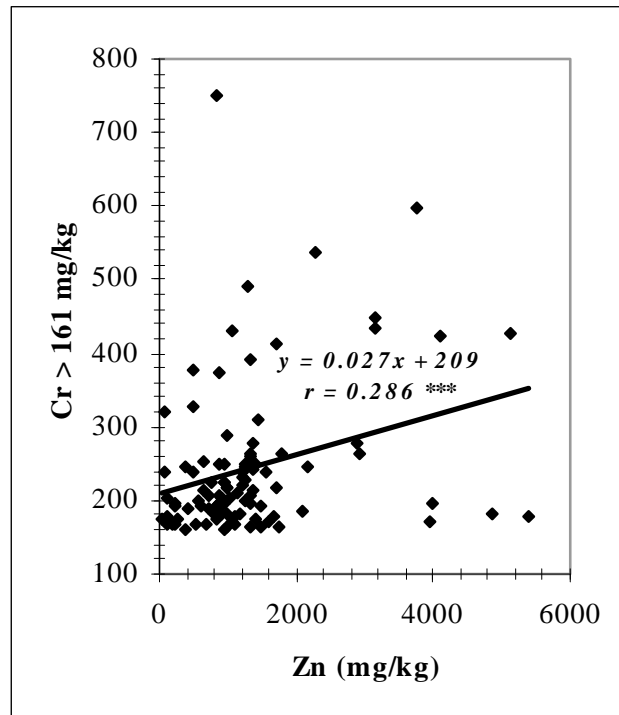


Figure 3



**Figure 4**

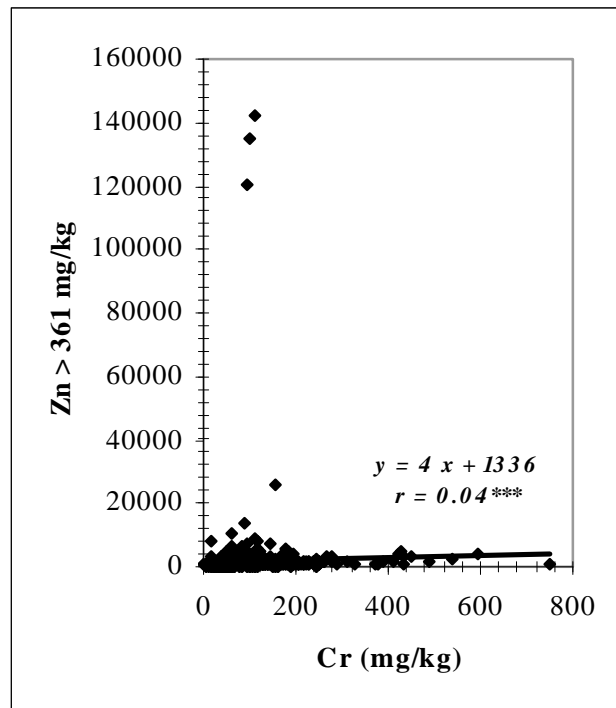




Figure 5

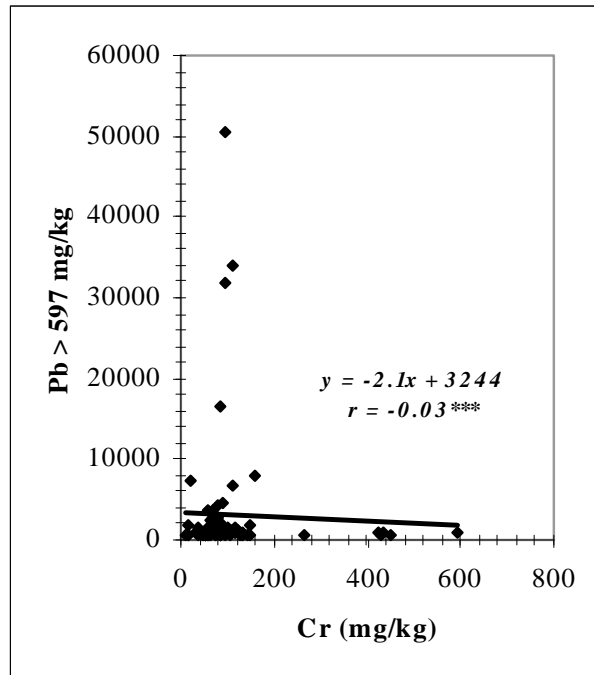
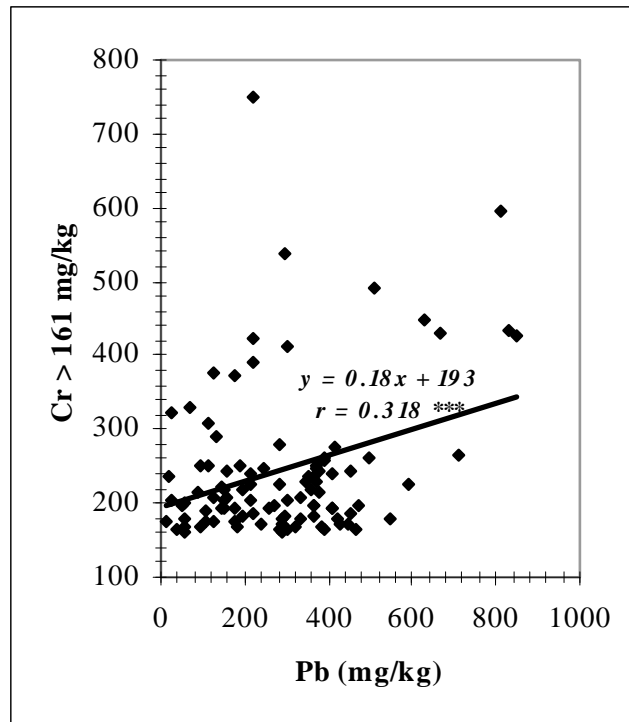


Figure 6





## Supplementary Material

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