CHARACTERIZATION OF CONTAMINATED SEDIMENT INCLUDING CONTAMINANT MOBILITY USING TCLP

John M. Carron, Laboratory Services Branch, Ministry of the Environment of Ontario, Canada

ABSTRACT
The investigation of a site for potentially contaminated sediment is shown through several different analyses for characterization and contaminant evaluation. In addition to bulk chemical analysis of the sediment for selected contaminants, several of the samples are further characterized for the possibility of producing toxic leachate as defined by Ontario Regulation 347. Established methods are applied in a unique and cost effective manner in order to characterize and evaluate potentially contaminated sediment.

RÉSUMÉ
L'enquête d'un site pour un sédiment qui pourrait être contaminé est montré par quelques analyses différentes pour leur caractérisation et pour une évaluation des polluants. En addition à une analyse chimique en masse de polluants sélectionnés, plusieurs des échantillons sont également caractérisés en tant que producteurs de lixiviat toxique tel que défini par les Consignes d'Ontario 347. Des méthodes établies sont appliquées dans une manière qui est unique et d'un bon rapport coût-efficacité pour caractériser et évaluer ce sédiment potentiellement contaminé.

1. INTRODUCTION

Background: the Ontario Ministry of the Environment is in the process of strengthening requirements for the treatment, movement and disposal of hazardous waste and implementing the framework for cleaning up contaminated lands.

Contaminated sediments pose the potential problem of continually contaminating the surrounding water. Removing the material may cause problems associated with stirring up the sediment and allowing it to mix with surrounding water and be carried away. Knowing what the contaminant in the sediment is and knowing if it will leach out of the sediment and into the surrounding water are two measurable situations that can be addressed. Bulk analysis will identify the amount of contaminant present, whereas leaching the sediment and analyzing the leachate will identify what contaminants are mobile and may therefore pose a problem if they leach from the contaminated material.

In this investigation, the sediment is known to be contaminated. It is considered waste. Is it hazardous or non hazardous? Can it be dredged and moved? By regulation, does it pass or fail the test for toxicity? If the waste were contained, or the contaminants bound up, contamination becomes less of an issue than when the contaminant can migrate and either leach into the surrounding water column or water table at a dump or landfill site after waste sediment is dredged up and moved. Waste samples that have been treated with lime, such that the final pH of a solution is over 12, often show no mobility for heavy metals such as cadmium, lead and chromium. In a few cases where waste has originated from metal plating operations, even after treatment the contaminant levels are not immobilized and the leachate exceeds the regulation level. Alba et al. (2001) discuss the use of Portland cement to immobilize heavy metals such as cadmium. Rho et al. (2001) discuss the use of reactivated or catalytic-activated carbon and hydrogen peroxide to reduce the leachability of both phenol and 2-chlorophenol. These approaches would be impractical when considering a large site area, especially sediment under water.

In addition to measuring the different chemicals that may be found in a contaminated sediment, it is also necessary to determine if they pose a hazard to the surrounding area, be it the water column in contact with the sediment or the landfill site, or waste repository where the material will be deposited after it has been dredged up and removed from its original location. Williamson et al. (2002) reported the migration of PAHs from spiked sediment through the water under laboratory conditions. PAHs are one of the contaminant groups studied here for mobility from the solid sediment to the liquid leachate. Carron et al. (2002) demonstrated a site specific volatile contaminant in sediment well above regulation guidelines.

A methodology which would be able to measure and predict the leaching of contaminants would be more cost effective than analyzing for all of the contaminants. Unfortunately, there is not one single test that will address all situations. For regulatory purposes in Ontario there is a test that evaluates 88 organic and inorganic parameters for their leachability in which regulatory levels are one hundred times higher than those used for drinking water. (Ontario Regulation 459/00). These contaminants are monitored as per Ontario Regulation 347, amendment 558/00, the Toxicity Characteristic Leaching Procedure (TCLP). Dredged sediment, if contaminated, would be a material that would not be acceptable for landfill if the material were shown to generate toxic leachate. Contaminated material that is treated or stabilized may pass a regulatory test, but without that test there would be no way to assess the potential leaching of contaminants from the waste material. For the present, TCLP does serve as a regulatory indicator of potential mobility for 88 contaminants, listed in Ontario Regulation 347.

One way to determine if a waste is hazardous or not hazardous is to measure some of its properties. In this case, toxicity is a property that will be measured by determining if target contaminants leach into an aqueous solution to produce a concentration that exceeds the Regulation contaminant level. A bulk analysis of the waste sediment indicates the target parameters that are available and their concentrations. Further investigation using TCLP determines the mobility of the contaminant which, if leached into the extraction fluid may produce a toxic leachate.

This paper presents the bulk analysis of several contaminated sediment samples and the corresponding TCLP results.

2. EXPERIMENTAL

Surface and core sampling have different requirements. Sample sizes are different. Sample integrity will certainly be different. The nature of the sample, the amount required, and the difficulty in obtaining the sample are just a few of the variables that come into play when sampling a specific site.

More than forty-six samples were used in this study in order to determine the boundary of the area being investigated and the distribution of contaminants in the sediment using both grab and core samples. A fairly large sample of several kilograms was collected in order to ensure homogeneity, representation of the immediate area, and also avoidance of sample loss due to the sample washing away from the sampling equipment. The surface/grab samples were taken with a Ponar dredge. This device grabs the sample and the immediate surface and lower layer are mixed. The sediment sample was pulled up in the dredge, excess water drained away from the device, leaving the bulk of the sediment intact. Core samples to a depth of one meter were taken with a Benthos core sampler. The core sample was protected from the surrounding water, remained intact and was an undisturbed sample. The sample core became mixed when pushed out of the sampler and into the sample container when two to four portions were taken to constitute a single sample. This amount of sample was sufficient to half fill a “Tox Pail”, which consists of a clean five gallon plastic pail with a food grade heavy duty polyethylene plastic bag liner. Double bagging was used; headspace was minimized when the bag was sealed.

After collection, the samples were sent to the laboratory for sub sampling. Specific target analysis dictates the correct choice of sample container. For example, organics are stored in glass and metals are stored in plastic containers. In this case the samples were stored in the original plastic bags for only a couple of days. In the laboratory, the “tox pails” were placed in a fume hood, opened and the plastic bag tie removed. Excess surface water on the sample was removed (wet sediment on standing will settle, forcing excess water to the surface), the inner portion was mixed using a large scoop to stir and blend the sample, which was then sub sampled. The sub samples were taken from the top inner portion of the container and transferred to glass jars and plastic bottles.

Sample portions taken for volatiles are stored in a glass jar which is completely filled and void of headspace. These sample portions are stored at 4^0 C and analyzed within less than the maximum holding time of 14 days. For the other sample portions the maximum holding time from sample collection to TCLP extraction is 14 days for semi volatile organics, 28 days for mercury and 180 days for metals.

Sample portions were prepared for specific analysis. Volatiles were sub sampled from the completely filled glass jar. Bulk metals were done on a dried, ground and sieved (40 mesh) sample portion. Sample portions for TCLP were pressure filtered in order to obtain the solid portion of the sample used to produce the leachate.

Bulk analysis measures the total contaminant present. TCLP measures the mobility of the contaminant, under specified conditions, as required by regulation. It should be pointed out that there is no defined percent recovery of contaminants in the TCLP method; recovery of a contaminant is sample dependent. A simplified approach, called the twenty rule, is used to determine if TCLP is required on a sample. The TCLP uses leachate made from the solid waste portion of the sample. One part waste is extracted with twenty parts leaching fluid. This amounts to a twenty fold dilution of the solid sample. Hence, one twentieth of the bulk value would have to produce a value greater than the leachate regulation concentration. If bulk analysis shows that this is impossible, using the assumption that one hundred percent of the contaminant were to leach, then there is no point in analyzing for that contaminant in the leachate.

Laboratory Services Branch Method E9002, “The Preparation of Leachates Using the Toxicity Characteristic Leaching Procedure (TCLP)” provides sample preparation techniques and lists all of the methods required to support the target contaminant analysis of 88 compounds routinely analyzed in our laboratory.

A unique scheme was worked out to provide regulatory monitoring in the most cost effective manner. Using the TCLP method, leachate was made and distributed for analysis by using the designated methods. To support the full TCLP analysis requires twenty analytical methods, sharing eight sample portions. The quickest analysis was done first: bulk screening for volatiles and analysis of leachate for metals. The last analysis, the most expensive and complex done, was for dioxin and furan. The rational for this approach is that it takes only one contaminant above regulation level for the sample to be considered leachate toxic. If and when an exceedance contaminant is found, the analytical process stops. This saves time and resources.

In order to appreciate the time and cost savings, volatiles can be analyzed using head space GC/MSD. Carron et al.

(2000) demonstrated that head space for volatiles in leachate is a better choice than purge and trap. Turn around time can be a little as one hour. Dioxin/furan require an extensive sample work up and require more than a couple of days to turn around. Our tests are applied in an innovative manner, doing the quicker, less expensive tests first. The analytical tests are sequenced through a fixed cycle, first doing volatiles, then metals, hydrides, boron, mercury, general chemistry (NTA, nitrogen, fluoride, cyanide), a GC/MS screening for semi volatile organics, followed by specific target analysis for selected pesticides and lastly dioxin and furan.

At the start of this investigation, initial bulk analysis was done in order to determine which of the sediment samples were best suited for the TCLP investigation, since only those samples that would produce a regulatory exceedance need to be considered. For practical purposes, only those bulk analysis indicating a level twenty times higher than the leachate concentration need to be investigated. Many of the analytical methods used are capable of providing several different tests; for example, analysis for metals, such as lead, provides additional non regulatory parameters, but at the same cost. Similarly, analyzing sediment for PAHs provides several targets in addition to benzo(a)pyrene (BAP), the only regulated PAH. Sediment samples were screened for volatiles but only those samples that could possibly provide an exceedance were considered before actually preparing leachate for the TCLP test using the ZHE (zero headspace extractor).

3. RESULTS

Total carbon (TC) and total organic carbon (TOC) for three representative sediment samples was found to be 160/130 , 190/170, and 130/100 TC/TOC, mg/g. One sediment sample screened for dioxin and furan had detectable levels for tetra, penta, hexa, hepta congeners, with a highest level of 320 pg/g octachlorfuran and 1800 pg/g octachlorodioxin. Leachate made from a similar sediment sample had no detectable levels of any of the congeners or octachlorofuran or octachlordioxin to a detection limit of 2 pg/L in leachate. Total Kjeldahal nitrogen in dry sediment ranged from 1.0 to 1.7 mg/g. Total phosphorous was 1.0 to 1.8 mg/g. Nitrogen as nitrate + nitrite in leachate was less than 100 mg/L, fluoride was less than 15 mg/L, total cyanide was less than 2 mg/L. An initial investigation of sediment from the site found methoxychlor at 140 ng/g. Later samples only detected 25 to 55 ng/g. The last survey of forty-six samples detected no methoxychlor above the detection limit of 5 ng/g.

This study of a large group of sediment samples identified many common contaminants consisting of metals, such as lead, volatiles such as benzene, semi volatiles such as pesticides (DDT), PCBs and PAHs. Not all of these contaminants are regulated, but, within each class of compounds, there is at least one contaminant that is regulated for mobility using TCLP.

From the study group, a few samples for metals were randomly selected and analyzed. Typical bulk concentrations ranged from: cadmium, 5.4 to 6.2 ug/g, arsenic, 13 to14 ug/g and selenium, 2.5 to 2.8 ug/g.

For the entire group of forty-six sediments, the following higher average bulk values were found: for metals, lead, 447 ug/g, chromium 84 ug/g; for volatiles, o-xylene, 932 ug/kg, m,p-xylene, 1458 ug/kg, ethylbenzene, 775 ug/kg, and benzene, 3174 ug/kg. PCBs averaged 654 ng/g. Also, semi volatiles were present in the following concentrations, ng/g: pp-DDE, 45, a-BHC, 3, b-BHC, 16, g-BHC, 6, a-chlordane, 6, g-chlordane, 13, oxychlordane, 238, op-DDT, 10, pp-DDD, 11, pp-DDT, 19, heptachlorepoxide, 4, endosulfan I, 8, dieldrin, 7, endrin, 25, endosulfan II, 9, and endosulfan sulfate, 36. The following PAHs were found in the sediment samples: naphthalene, acenaphthalene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo (b) fluoranthene, benzo (k) fluoranthene, benzo (a) pyrene, indeno (1,2,3,-c,d) pyrene, dibenzo (a,h) anthracene, and benzo (g,h,i) perylene. Concentrations for these PAHs ranged from over one thousand to several tens of thousands of ng/g. The only regulated PAH is benzo (a) pyrene (BAP) which had an average bulk level of 24,000 ng/g.

Within the group of sediment samples there are both grab and core samples. Bulk average values for several semi volatile organic contaminants for the core samples show an overall average value that is higher than the average value found for the grab samples (Table 2). The overall average ratio of core average to grab average is 3.5 for all the contaminants shown. This average takes into account two metals, lead and chromium, that were only ten percent higher in the core samples, and the volatiles where the difference was almost ten times higher; the core samples had an average of 8.1 mg/kg benzene. Two semi volatiles, pp-DDE and oxychlordane were four times higher in the core samples, when compared to the average surface or grab sample.

Reviewing the bulk sample analysis data revealed that there were only three samples that had a bulk level high enough to warrant TCLP follow up. Zero headspace extraction (ZHE) confirmed that benzene did leach and exceed the regulation limit of 0.5 mg/L. Further repeat analyses were done in order to provide a degree of confidence for monitoring the mobility of benzene in the solid sediment. Method performance depends on several variables. In this particular set of samples, the matrix was the greatest variable and benzene was the only exceedance noted. There was only this one regulatory contaminant to define the waste sediment as being “toxic”.

To demonstrate the method performance and the degree of confidence for the analysis with this sample matrix, the original tox pail was re sampled and 10 portions of fresh sample were removed; further sub portions were taken for volatile analysis. The precision for the analysis of this contaminated sediment sample was found to be 0.817 (+/- .034) mg/L benzene (Carron et al. 2002).

While none of the targeted compounds other than benzene leached to produce an exceedance, it is interesting to note that the high level of PAHs did produce trace levels in the leachate. Values ranged for the following: phenanthrene was found at 5.9 to 28.2 ug/L, anthracene, 1.1 to 5.3 ug/L, fluoranthene, 1.1 to 2.9 ug/L, pyrene, 0.6 to 1.5 ug/L, benzo(a)anthracene only at 0.01 ug/L, and chrysene, 0.04 to 0.09 ug/L.

Three acid herbicides were found at trace levels in leachate: dicamba, 0.025 ug/L, MCPP, 0.328 ug/L, and 2,4-D, 0.262 ug/L.

Very little metal leached from the sediment samples. For example, a couple of chromium leachate concentrations at mg/L when compared to the bulk at ug/g total gave the following ratios, 0.11/119, 0.8/107 and for lead, 0.31/819, 0.07/317. Less than one percent of the bulk metal leached, which is not surprising since lead and chromium are very stable and weather well.

PCBs ranged from 260 to 1200 ng/g (dry sediment).

4. DISCUSSION

Why are we only monitoring a limited number of contaminants? In practice, landfill sites designated for accepting waste material, know their “clients”. Certain waste streams always originate from the same process. For example, a metal plating waste stream will always have chromium; a contaminant such as DDT would never be expected. Therefore there is no need to monitor a metal plating waste for DDT. This fact lends justification to the initial screening process which relies on bulk analysis, and monitoring only the regulated contaminants using TCLP. In the case of this study of contaminated sediment, bulk analysis found several contaminants covering a broad range of chemicals.

One of the most toxic contaminants, benzo(a)pyrene (BAP), is shown to be present at an average of 24000 ng/g in the sample group. Leaching the sample produced a leachate that did not contain a detectable amount of BAP. Since this is the only PAH that is specified by Regulation 347, and the sediment was found to contain significant amounts of this known carcinogen, further investigation was warranted. BAP is almost insoluble in water, hence the low limit of .001 mg/L (1 ppb) in leachate. PAHs also tend to adsorb onto the laboratory glassware and equipment that they come into contact with during sample work up. Was the non detectable level of BAP due to loss during sample extraction? The samples did contain a high percentage of carbon, the sediment itself was fine particulate matter, both conditions possibly favoring adsorption of the PAHs. In order to rule out the possibility of loss on glassware during extraction and handling in the laboratory during sample work up, a repeat extraction on three sample portions was done. The samples were leach extracted from glass bottles that were silanized to minimize adsorption during extraction of the sample. The repeat analysis showed no detectable levels of BAP. The BAP in the sediment does not leach to produce a toxic leachate for these sediments.

Hexachlorcyclohexane consists of several isomers. The isomer, gamma BHC, is often referred to as lindane and accounts for about 15% of the mixture. The alpha isomer accounts for 65 to 75% and the beta isomer accounts for 7 to 10 % of the technical grade mixture. BHC is strongly adsorbed on soils; environmental degradation occurs under anaerobic conditions. Results from the core samples found an almost opposite distribution when compared to the technical mixture: alpha 4 (13%), beta 20 (65%), and gamma 7 (22%) ng/g average. The total concentration in the sediment was highest in the core samples. Similar ratios of the alpha, beta, and gamma were found in both the grab and sediment samples, with the exception that the alpha isomer in the grab sample was slightly lower and the gamma just slightly higher.

Table 1. Distribution of BHC Isomers

contaminant	LD 50	grab sample ng/g,	%	core sample ng/g,	%
alpha BHC	500	2	8.7	4	13
beta BHC	6000	15	65	20	64.5
gamma BHC	125	6	26	7	22.5
Total BHC		23	100	31	100

Further consideration of the TCLP Regulation in addressing only lindane, even though it is not the most predominant isomer, is the fact that it is forty eight times more toxic than the beta isomer. The more toxic and hazardous contaminant is clearly the best choice to regulate.

Additional data are presented in Table 2. The overall average levels for the DDT, DDD and DDE are similar in the grab and core samples with the exception of pp-DDE which is six times higher in the core. The de-hydro chlorination (loss of HCL) of DDT leads to DDE. The higher level of DDE in the core samples may reflect the metabolic breakdown of the DDT to a more stable metabolite in the anaerobic conditions of the sediment.

Two isomers of chlordane are found in a similar ratio in both the grab and core sample averages. Figure 1 shows that the metabolite, oxychlordane is present at ten times the total chlordane in the grab sample and sixteen times the total chlordane in the core sample. The core sample contains four times the level of oxychlordane, compared to the grab sample, indicating that the metabolite is more stable under anaerobic conditions.

The average PCB level of 832 ng/g dry sediment (core samples) was significantly higher than the 607 ng/g average concentration found in the grab samples. This may suggest that up to 200 ng/g PCBs was washed away with water in contact with the sediment. The concentration of PCBs varied from sample to sample, there was no uniform or constant concentration, but rather many highs and lows. Lower PCB levels were found in samples with high benzene levels. To exceed the regulatory limit, the sediment would have to contain 6 mg/g, with all the PCBs being leached. No PCBs were identified in the leachate above 0.03 mg/L.

Two of the regulated metals, lead and chromium, leached only trace amounts. The sediment analysis shows that the concentration of chromium in the grab and core samples is very constant across all samples taken. There is very little difference from one sample site area to another. This is sharply contrasted with the bulk lead values which fluctuate from 219 to 861 ug/g of dry sediment. There does not appear to be any correlation between the sample site values.

Chlorinated dioxin and furan were found at concentrations of less then 2 pg/L in the leachate. This is far below the regulation level of 1500 pg/L.

The contaminated sediment was found to contain very high levels of PAHs. This may have originated from past dumping practices. Pesticide analysis identified several chlorinated pesticides that may have been buried as deep as one meter. These contaminants reflect possibly long term run off. They appear to be entrapped within the silt and show little mobility. Additionally, pesticides such as DDT have been banned for many years, again suggesting an old long term deposit.

5. CONCLUSION

Characterization of the sediment samples using bulk analysis determines what contaminants are present and their concentration. This provides information about the contaminants present, but only suggests what might be a hazard. To demonstrate that the sediment is not only contaminated, but hazardous requires additional testing. Applying the TCLP test confirms that the initial suggestion of a hazardous waste is proven. The contaminated sediment produced a toxic leachate. Benzene was shown to be produced in exceedance of the regulation concentration of 0.5 mg/L. What may have initially been assumed, perhaps, that benzo(a)pyrene was the contaminant that would make the waste hazardous is demonstrated to be of secondary concern as the leachate concentration was below regulation level for this regulated PAH. Several pesticides were identified, and higher levels were found in core samples than in grab samples indicating a long term build up. Leaching the sediment failed to leach any significant amount of the entrapped pesticides, indicating that they had little or no mobility. Application of the TCLP test provides a regulatory tool to monitor the mobility of a contaminant that may have the potential to generate a hazardous waste.

6. ACKNOWLEDGMENTS

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Table 2. Examples of Contaminants Found in Core Samples.

contaminant	A	B	C	overall average	grab average	core average	core/grab ratio
chromium, mg/g	85	119	107	83.7	82.8	87.3	1.1
lead, mg/g	61	819	511	446.7	427.7	518.7	1.2
benzene, ug/kg	5800	20000	11000	3174.0	706.0	8110.0	11.5
ethylbenzene, ug/kg	5000	1700	830	775.2	264.2	1746.0	6.6
m,p-xylene, ug/kg	1000	15000	8300	1457.8	371.5	4282.0	11.5
o-xylene, ug/kg	6200	8000	4800	932.2	227.3	2765.0	12.2
PCBs, ng/g	720	1200	920	654.2	607.4	832.0	1.4
a-BHC, ng/g	4	7	2	2.7	2.4	3.6	1.5
b-BHC, ng/g	22	39	26	15.7	14.5	20.0	1.4
g-BHC, ng/g	5	11	13	6.4	6.0	7.1	1.2
a-Chlordane, ng/g	8	10	ND	5.6	4.2	8.0	1.9
g-Chlordane, ng/g	32	64	48	13.5	8.6	28.6	3.3
oxychlordane, ng/g	570	1400	1100	237.7	140.1	608.6	4.3
pp-DDE, ng/g	100	250	200	44.5	20.4	121.6	5.9
op-DDT, ng/g	10	10	ND	10.0	10.0	10.0	1.0
pp-DDD, ng/g	ND	ND	10	11.3	10.0	11.7	1.2
pp-DDT, ng/g	20	80	25	18.9	14.6	25.6	1.7
heptachlorepoxide, ng/g	3	10	8	4.4	2.6	6.1	2.4
endosulfan I, ng/g	8	14	14	7.8	4.6	11.8	2.6
dieldrin, ng/g	6	16	14	6.6	5.6	9.8	1.7
end in, ng/g	48	80	100	25.2	18.7	47.6	2.5
endosulfan II, ng/g	8	ND	8	8.6	8.0	9.0	1.1
endosulfansulfate, ng/g	80	160	100	36.2	27	69.4	2.6
benzo(a)Pyrene, ng/g	30000	110000	61000	23870.8	18750	43330	2.3

ND is not detected
The average ratio of core average to grab average is 3.5

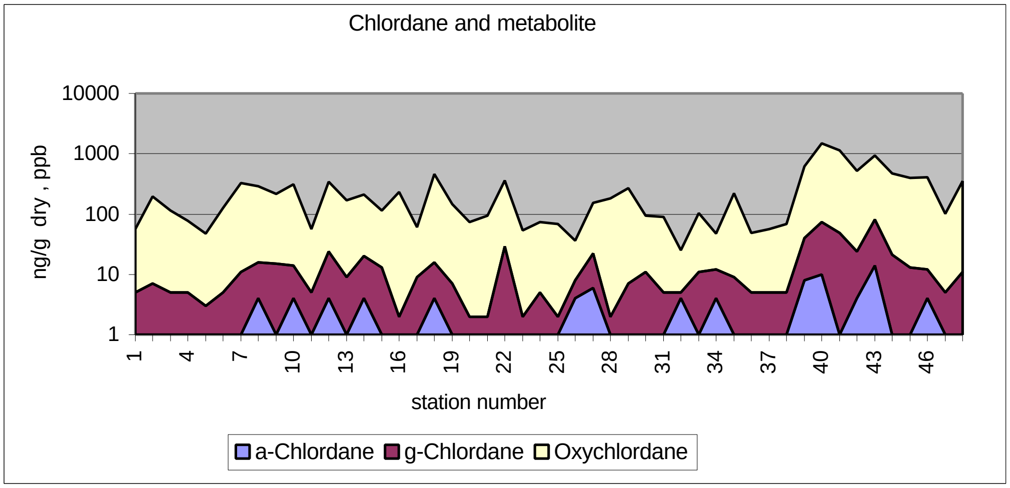

Figure 1. Distribution of chlordane in grab and core samples.