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LEVELS, PERSISTENCE AND BIOAVAILABILITY OF ORGANIC CONTAMINANTS PRESENT IN MARINE HARBOR SEDIMENTS IMPACTED BY RAW SEWAGE

Jocelyne Hellou[1*], Donald Mackay[2] and Joseph Banoub[3]

1.Science Branch
Department of Fisheries and Oceans
Bedford Institute of Oceanography
P.O. Box 1006
Dartmouth, Nova Scotia
B2Y 4A2 Canada

2.Trent University
Environmental and Resource Studies
Peterborough, Ontario
K9J 7B8 Canada

3.Science Branch
Department of Fisheries and Oceans
P.O. Box 5667
St John's, Newfoundland
A1C 5X1 Canada

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*To whom correspondence should be addressed

Abstract:

As part of a program to investigate the levels, fate and bioaccumulation of organic contaminants in a polluted marine harbor, organochlorine compounds including the polychlorinated biphenyls (PCBs), dichloro diphenyltrichloroethane and metabolites (DDTs), chlordanes, dibenzo-p-dioxins (Ds) and dibenzofurans (Fs), polycyclic aromatic hydrocarbons (PAHs) and sulphur hetero cycles were analysed in sediments spiked with St. John's Harbor sludge. Winter flounder (*Pseudopleuronectes americanus*) were exposed to these sediments containing six levels of harbor sludge during four winter months. Following exposure, sediments were reanalysed to investigate the persistence of the contaminants. The primary contaminants detected were PAHs (~5000 ng/g), predominantly alkylated phenanthrenes, fluoranthene and pyrene; PCBs with a predominance of Aroclor 1260 signature (~64 ng/g), DDTs (~5 ng/g), hepta and octachloro dioxins and furans (~0.5 ng/g) with very low levels of less chlorinated congeners. The PAHs degraded with an estimated half life of 2 to 3 months, while no significant degradation could be attributed to the other compounds. Bioaccumulation to muscle showed the potential uptake of contaminants in biota inhabiting the harbor. A dose-response relationship was observed between spiked sediments and the concentrations of PCB congener 153 and unresolved congeners 138/163/164 in muscle. Of the dioxins and furans, only 2, 3, 7, 8-tetrachlorofuran was detectable in muscle and at a similar concentration in all exposures indicating a similar bioavailability independent of the fraction of sludge in sediments. Of the PAHs, only naphthalene and methyl naphthalenes were detected in muscle, but did not display a dose-response. One bile metabolite of pyrene was quantified and demonstrates metabolism. Biota-sediment accumulation factors were of 0.2 to 7 indicating that equilibrium was approached, with the exception of the hepta and octachloro dioxins and furans which were not significantly bioaccumulated.

Introduction:

Urban communities which discharge treated or untreated aqueous effluents to the marine environment can have profound effects on the quality of water, sediments and biota. Of particular concern is the contamination of finfish and shellfish, which are in intimate contact with sediments containing organic chemicals and metals of anthropogenic origin. The toxicity of sewage sludge has been documented for a number of aquatic species, at several life stages and over a range of acute or chronic exposures resulting in a variety of toxic effects [e.g. 1, 2]. Benthic communities have been characterized, including triad studies relative to distance from sewer outfalls [e.g. 3-7]. The 96 h LC_{50} of sewage sludge ranges from 0.0003% to 20%, in terms of volume of sludge to seawater, with toxic concentrations generally below 1.0% [2]. Long-term studies have shown toxicity at levels of exposure lower by orders of magnitude, than short-term studies.

The present study seeks to document the nature and concentration of organic contaminants in harbor sediments impacted by untreated sewage and urban road runoff. Further, the persistence of these contaminants is assessed over a four months period, and their potential for bioaccumulation is determined under laboratory conditions using winter flounder (*Pseudopleuronectes americanus*). Gall bladder bile was also examined for the presence of metabolites.

Winter flounder were chosen because they are dormant during the winter, when they have lower respiration rates and they naturally do not feed, as detailed in [8]. They are ideal marine vertebrates for long-term exposures in which variables such as feeding, movement and stress are minimized. Whereas most uptake and toxicity tests employ contaminated water or food as the exposure medium, in this case the complexity of the mixture of chemicals, the choice of experimental organism and the significant differences in bioavailability of sediment-bound substances dictates that exposure should be to the sediment. As well, caging fish would have been impossible due to the anoxic harbor sludge.

Muscle tissue was analysed because fillets are of commercial interest and available in larger quantities than liver which is preferable for biochemical analyses although concentrations in that organ would be expected to be higher than in muscle [9]. The experiment does not simulate actual exposure conditions because of our inability to reproduce the actual environmental variables (poor water quality: e.g. oxygen, pH, coliform bacteria).

Materials and Methods:

Sludge was collected from St. John's Harbor (Newfoundland) and mixed in various proportions (0, 1, 2, 5, 10 and 20%, volume:volume) with uncontaminated sediments collected from a remote beach and placed in separate tanks (45 kg sediments, 300 L water, 12 h light/dark, T=1-3^0 C, continuous aeration). Winter flounder were added to the six tanks, referred to as E-0 or reference, E-1, E-2, E-5, E-10 and E-20 and exposed from early February to early May 1994, in the Ocean Sciences Laboratory. Flounder were not fed during the experiment since they were naturally dormant.

Sediments from each tank were subsampled in triplicate at the beginning and end of the exposure and composite samples analysed. Linear regressions between the concentration in spiked sediments and percent sludge were used to deduce concentrations in harbor sludge (r=0.91-0.99, n=4-6, all better than 1% level of significance), since the original sample of harbor sludge was not available. Briefly, PAHs were extracted from sediments using a Soxhlet apparatus (after drying and mixing with sodium sulfate) and from wet tissue using caustic digestion (50% KOH in MeOH:H2O, 10]). They were purified on a silica column and quantified by GC-MS (multiple ion monitoring: MIM; 2 ions/compound), using a DB5 column (30 m, 0.25 mm, 0.25 μm). The following compounds were analysed: naphthalene (NA) and C-1 to C-4NA, acenaphthylene (AY), acenaphthene (AE), fluorene (F), phenanthrene (PA) and C-1 to C-4PA, dibenzothiophene and C-1 and C-2DBT, anthracene (A), fluoranthene (FL), pyrene (PY), benz(a)anthracene (BA), chrysene (CH), benzofluoranthenes (BF), benzo(e)pyrene (BeP), benzo(a)pyrene (BaP), dibenz(a,h)anthracene (DA), benzo(g,h,i)perylene (BP) and indenopyrene (IP). The mean recoveries of 10 deuterated surrogate standards (parental PAH) present in each sample varied between 64 and 90%, while measured vs expected concentrations of PAHs in standard or spiked reference materials generally overlapped.

Chlorinated dioxins (Ds) and furans (Fs) were extracted by mixing tissue and anhydrous sodium sulphate and extracting with dichloromethane : hexane [11]. Purification took place by a 4 steps column chromatography while quantification was performed by HRGC-MS (MIM, 2 ions/compound) using a DB5 column (60 m, 0.25 mm, 0.1 μm). Other OC contaminants were purified on a Florisil column, less polar compounds (hexane eluent) were analysed by GC-MS and the more polar fraction (dichloromethane: hexane, 1:1) by GC-ECD, using the last described columns [12]. The following compounds were analysed: α, β, and γ-HCH; HCB; oxychlordane; trans- and cis-nonachlor and chlordane; heptachlor; heptachlor epoxide; methoxychlor; o,p'- and p,p'-DDE,

DDT and DDD; mirex; dieldrin; endrin; aldrin and PCBs measured as Aroclor standards (1242, 1254 and 1260). The mean recoveries of 5 carbon labelled surrogate standards present in each sample ranged from 62 to 77%, while measured vs expected concentrations in standard reference materials were between 43 and 130% (mean: 70%). A series of 17 Ds and Fs substituted at C-2, 3, 7, 8 and total tetra-, penta-, hexa-, hepta- and octa-chlorinated was also analysed. The mean recoveries of 5 carbon labelled Ds and 4 Fs surrogate standards present in each sample ranged from 66 to 88%, while measured vs expected concentrations of Ds and Fs in standard reference materials ranged from 61 to 130% (mean: 94%). PCBs were quantified as 80 congeners, including 12 unresolved groups.

The protocol included the processing of a blank, a duplicate and the analysis of a standard reference material or spiked matrix with every batch of 3-8 samples. Each sample also contained labelled surrogate standards that allowed to determine recoveries and adjust concentrations. Detection limits (DL) varied but were generally between 0.1-0.6 ng/g, for OC pesticides and of 0.5-2.5 ng/g for the Aroclors. For dioxins and furans, DLs increased with higher chlorination: 0.1-0.9 pg/g. The DLs were between 0.1-0.8 ng/g for PAHs and between 0.01-0.15 ng/g for specific PCB congeners. Analyses were performed by Axys Analytical Services, Sidney, British Columbia.

Lipid content was determined gravimetrically by evaporating a subsample of dichloromethane:hexane (1:1) tissue extract. All concentrations are expressed in terms of wet weight and can be converted to dry weight, using a moisture content of 80% for muscle and 14% for sediments. Dry weight were determined by subsampling the sediments or muscle tissue and drying at 100^{0}C for 20-24 hrs. The density of the sediments collected at the end of the four months was 1.9 kg/L and the pH was neutral. The particle size distribution was very coarse and similar in all tanks, with a 1% fraction below 63μm, 78% between 63 μm and 2mm and 21% between 2 mm and 1 cm.

Equal amounts of muscle tissue were dissected from each of ten fish per tank after four month's exposure. The content of the gall bladder bile (equal volume/fish) pooled from the same 10 fish was also examined after enzymatic hydrolysis. Enzymes deriving from limpets containing β-glucuronidase and sulfatase (800 units/ 100 μl bile) were used as described in [13]. Following solvent partitioning, analysis of oxidized xenobiotics was performed by ultra-violet fluorescence (uv/f) at the phenanthrene and chrysene wavelength pairs (313/374 and 310/360nm, respectively) and by GC-MS after acetylation of the extracts [13].

Results and Discussion:

Contaminants detected in harbor sludge:

It is first useful to identify and list the contaminants which are likely to be found in sediments impacted by an urban community such as St. John's. Most contaminants enter the water in sewers or by direct discharges, but there may be additional discharges. The sewer system of St. John's, Newfoundland services a population of approximately 130,000 inhabitants and no major chemical industries. The full results of the analyses of the sediments and biotic samples are available [14].

Control sediments (E-0) analysed from the beginning of the experiment contained non-detectable levels of dioxins and furans (Figure 1). The concentration of Ds and Fs in the original sludge was estimated, not measured, by a linear regression between the level of octaD and the percent sludge. The key chemical species indicative of the presence of dioxins and furans in sediments are the octa and hepta chlorinated compounds. The source of these compounds has been attributed to combustion processes, industrial processes using chlorinated hydrocarbons and to pulp mill effluents using chlorine bleach [15]. In this harbor, they originate mainly from combustion processes, as confirmed by comparison of the fingerprint with published environmental data [16].

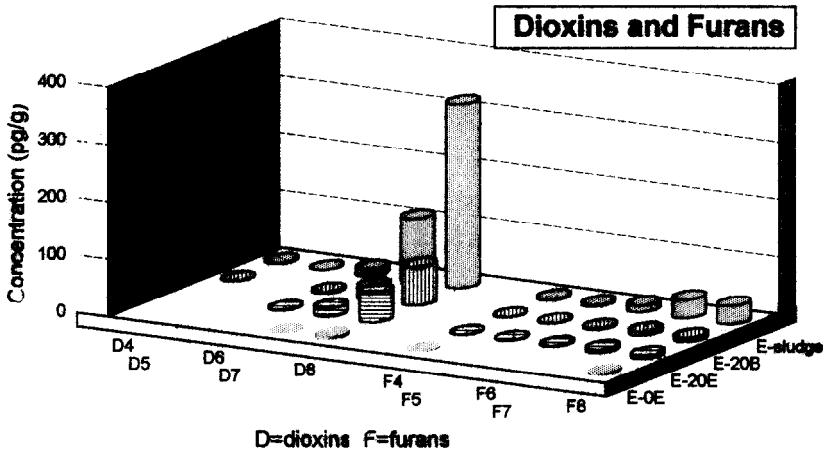


Figure 1. Polychlorinated dibenzo-p dioxins (D) and polychlorinated dibenzofurans (F) in sediments from the beginning (E-20"B") and end (E-20"E") of the exposure and deduced for original sludge. Numbers after D and F represent the number of chlorine atoms, while numbers following "E-" in the legend reflect level of sediment exposure.

Spiked sediments analysed at the beginning of the experiment contained mainly non-detectable concentrations of a series of OC compounds. The exception is PCBs, which were detected in all samples and p,p'-DDE and p,p'-DDD detected in E-20 sediments (0.3 and 0.7 ng/g). PCBs were measured as Aroclor standards and as specific congeners (Figure 2). The concentrations in the original harbor sludge were deduced to be approximately 64 ng/g of PCBs expressed in terms of Aroclor 1260 and approximately 1.4 and 3.3 ng/g of p,p'-DDE and p,p'-DDD, respectively.

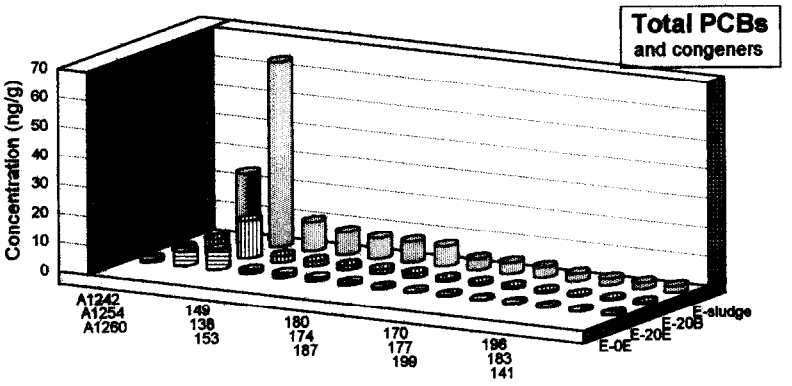


Figure 2. Polychlorinated biphenyls (PCBs) as total PCBs expressed as Aroclor standards (A1242, A1254 and A1260) and as specific IUPAC congeners in sediments from the beginning (E-20"B") and end (E-20"E") of the exposure and deduced for original sludge. Numbers following "E-" in the legend reflect the level of sediment exposure.

As expected, much higher levels of PAHs were detected in harbor sludge at approximately 5000 ng/g or 5μg/g for total PAH (sum of target compounds) with concentrations of 360 and 510 ng/g for phenanthrene and pyrene, respectively (Figure 3).

In summary, the contaminants detected in harbor sludge were dioxins and furans, primarily hepta and octa chlorinated compounds, at nearly 0.3 ng/g, PCBs at 64 ng/g, if expressed as Aroclor 1260, DDTs at 5 ng/g and PAHs at 5000 ng/g, with alkylated phenanthrenes, fluoranthene and pyrene being the primary components.

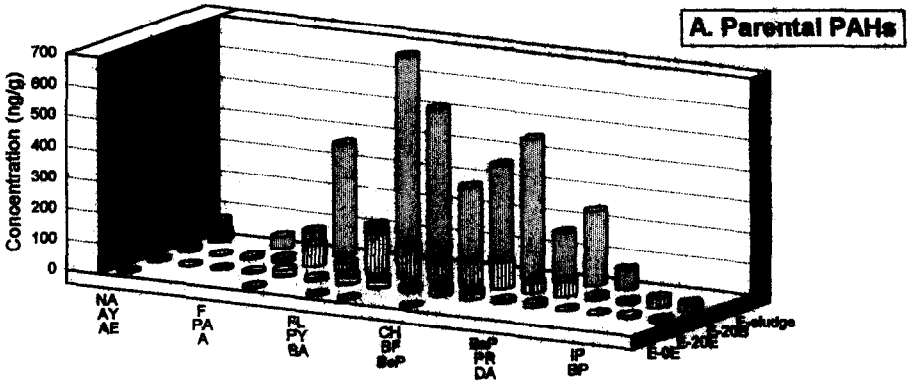
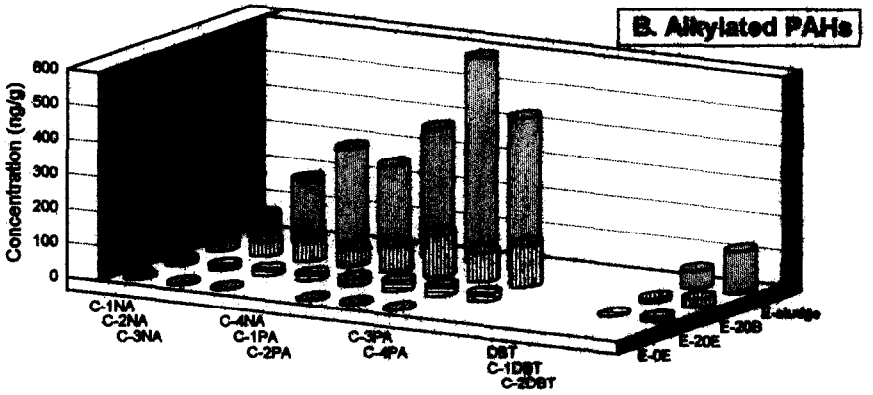


Figure 3A. Parental polycyclic aromatic hydrocarbons (PAHs) and B. Alkylated polycyclic aromatic hydrocarbons (PAHs) in sediments from the beginning (E-20"B") and end (E-20"E") of the exposure and deduced for original sludge. Numbers following E in the legend reflect the level of sediment exposure. The PAH abbreviations are defined in the Experimental section.



Persistence

Initial levels of contaminants were compared with levels four months later to determine losses by biotic and abiotic degradation and by dissolution in water which flowed through the experimental system. Concentrations of the predominant D and F congeners, i.e. 7D, 8D and 8F decreased by a factor of two, in the four highest exposures. The 1, 2, 3, 4, 6, 7, 8-heptachloro-D and F represented

50% and 35% of the total heptachlorinated congeners, respectively, with values similar to those before weathering. In some cases, certain congeners present at low levels showed an apparent increase in concentration probably because of the retention of contaminants present in the water intake to the tanks. There may be a higher concentration of hydrophobic contaminants in the near shore water of the Ocean Sciences Laboratory relative to the more remote location where the sediments were collected.

Table 1

Concentration of PAHs detected in all sediments (ng/g, wet)

	Begining							End						
PAH	E-0	1	2	5	10	20	sludge*	E-0	1	2	5	10	20	sludge*
Naphthalene	0.2	2	ND	6.8	7.6	13.8	65	0.3	0.6	0.7	1.1	1.2	4.1	18
C-1naphthalene	3.8	7.3	4.3	13	16	23	100	3.4	4.6	3.8	4.5	6.5	10.2	36
C-2naphthalene	4.0	7.9	5.3	14	24	39	166	3.2	4.8	4.4	5.1	6.5	11.8	43
C-3naphthalene	2.4	7.6	7.5	17	37	58	286	2.6	4.1	3.9	4.4	5.7	15	59
Phenanthrene	1.5	5.8	8.3	22	46	71	360	1.8	3.6	3.8	5.5	23	21	115
C-1phenanthrene	2.7	6.5	12	19	47	74	368	2	4.1	4.7	5.7	11	18	80
C-2phenanthrene	5	11	ND	29	74	120	595	3.8	6.1	6.3	9.7	12	27	113
Fl uoranthene	1	9	14	35	85	130	670	1.3	5.5	6.3	11	14	28	124
Pyrene	0.8	6.9	14	27	65	100	510	0.9	4.2	4.7	7.9	9.1	28	123
Chrysene	0.2	4	13	16	40	72	360	0.3	1.8	3	5.4	9.1	22	102

*Concentrations determined in E-0 to E-20 are used to deduce the value in harbor sludge (100%)

After four months, most OC pesticides were still non-detectable in sediments. Levels of p,p'-DDE, -DDD and -DDT were at nearly the same concentration as in the corresponding earlier sediments, with levels in E-0 to E-10 sediments remaining close to detection limits (0.1-0.3, 0.1-0.3 and 0.3-0.4 ng/g, respectively).

Concentrations of PCB congeners were very similar in sediments E-2, E-5 and E-10 after

four months, displaying a mean level of 0.2 ng/g for congeners 149, 138/163/164, 153 and 180 and of 0.1 ng/g for congeners 174, 170/190 and 118. Given the variability in the analyses and the possibility of some OCs becoming irreversibly bound to sediments, it is concluded that there was no significant loss of OCs for this four months period. This is in accord with other reports of long-term contamination of sediments by these persistent substances [e.g. 17-18].

After four months PAHs, however, showed a three fold mean reduction in concentration (range 1.1-7.1) compared to the beginning of the experiment (Table 1 and Figure 3). The PAH concentrations and fingerprint in control sediments from the beginning and end of the four months period, were similar, but different from harbor sludge. A consistently greater loss was observed at the two highest exposures for PAHs with increasing alkylation within the naphthalene and phenanthrene group. If the loss was by dissolution in water, less loss would be expected for the more alkylated PAHs since they have lower water solubilities and octanol-water partition coefficients. For example, the mean log K_{ow} of C-1 and C-2 naphthalene is 3.86 and 4.37 [19]. Biodegradation rates are also faster for lower molecular weight (MW) compared to higher MW PAHs. Loss could therefore be due to the transport of particulate and colloids from the sludge, where higher MW PAH would be preferentially absorbed. After four months, concentrations of C-1, C-2 and C-3 naphthalene, in E-1 to E-5 sediments were similar to control sediments, while concentrations of higher molecular weight PAHs remained higher than in the control. This indicates that PAHs with a higher K_{ow} than the naphthalenes were not introduced from the water intake. The bioavailability of PAH varies with the type and possibly source of hydrocarbons [e.g. 20-22] and those present in St. John's harbor have been assigned to combustion and petroleum sources using carbon isotope analyses [23].

These results indicate either a degradation half life of 2 to 3 months for all the PAHs, or alternatively more rapid and variable degradation rates of an available fraction of approximately 75%, or a combination of the two. In any event, there is a significant reduction in the quantity of available PAH in four months suggesting that most contamination in the sludge is of fairly recent origin.

Bioccumulation in winter flounder

The contaminant levels in muscle tissue are evaluated as wet weight concentrations and as biota-sediment accumulation factors (BSAFs). If equilibrium is achieved between the muscle tissue of lipid content L (g/g) and the sediment of organic carbon content OC (g/g), then it is expected that

$$BSAF = C_F / C_S = L \cdot K_{ow} / (K_{oc} \cdot OC)$$

where C_F and C_S are the wet weight concentrations of the contaminant in fish and sediment, respectively; K_{oc} is the octanol-water partition coefficient. If, as discussed by Mackay [24], K_{oc} is assumed to be 0.4 K_{ow}, then for OC content of 1 and 10% (lowest and highest expected values), L of 0.006 (observed mean), then the expected BSAF range from 0.15 to 1.5. For non-metabolizing chemicals a BSAF in the range of 0.15 to 1.5 is thus expected provided that there is sufficient time for equilibration.

Table 2

Contaminants in sediments and muscle of winter flounder

Chemical	log K_{ow}[1]	Sediments concentration[2]					Muscle conc.[2]		BSAF[3]
		E-10		E-20		Sludge	E-10	E-20	
		B[4]	E[4]	B[4]	E[4]				
4F	6.1	0.4	0.3	0.7	0.2	2.8	0.3	0.3	1-1.5
8D	8.2	57	28	66	51	320	ND	ND	ND
#153	6.9	0.9	0.5	1.4	1	6.9	1.8	1.2	1-3
#138(/163/164)	6.8	0.9	0.5	1.6	1.2	7.5	1.4	1.0	1-3
#118	6.7	0.2	0.1	0.4	0.4	1.8	0.7	0.6	1.5-7
Naphthalene	3.4	7.6	1.2	14	4	65	6.7	5.4	1-5
C-1Naphthalene	3.9	16	6.5	23	10	100	2.5	2.6	0.2-0.3

1-Recommended values in Tables 2.2 and 4.2 [19, 24]. 2-Concentrations are in ng/g, except dioxin (D) and furan (F) are in pg/g (wet). 3-BSAF: biota-sediment accumulation factors. 4-B and E: beginning and end of the experiment. ND: not detected and # refers to PCB IUPAC congeners.

Analysis of muscle tissue (Table 2) showed the presence of only trace amounts of 4F in all exposures, with the 2, 3, 7, 8 congener representing 100% of the total concentration (0.2-0.3 pg/g). The BSAF was in the expected range, about 1.0. It can therefore be concluded that 2, 3, 7, 8-tetrachloro-F is the most bioavailable of the D and F congeners present in harbor sludge. The more

predominant hepta and octa chlorinated congeners are not apparently bioavailable, at least in a four month exposure period. However, the low water solubility and high K_{ow} suggests that equilibrium may not be reached in muscle, after four month exposure (log K_{ow} = 5.8-7.7, 6.1 recommended for 4F, in [24]). On the other hand, the mean observed muscle concentration and BSAF for 4F is nearly similar in all exposures. Therefore, it must be concluded that the level of bioavailable furan is similar for feral and exposed finfish. The BSAF would also be nearly 1 if concentrations are expressed in terms of lipid weight for biota and expected organic carbon content for sediments (Table 2, if approximate lipid content and OC at 1%, each).

Although slightly more OC compounds were detected in muscle (mean of 0.6% lipid), including p,p'-DDE, trans-nanochlor, cis-chlordane, HCB, α-HCH and dieldrin (mean of 2.0, 1.2, 0.8, 0.6, 0.6 and 0.5 ng/g, respectively), all concentrations were below 8 ng/g. No clear bioaccumulation relationship could be observed for these compounds due to their high K_{ow} leading to a long time to reach equilibrium [25, 28]. Uptake through respired water represents the only route of exposure for flounder in the winter, since they do not feed. Although small amounts of sediment have occasionally been observed in the stomach of flounder, this intake would be expected as minor compared to the volume of water respired every day.

Aroclor 1254 : 1260 : 1242 were present in a 4 : 2 : 1 ratio in fish muscle from the three higher exposures (mean of 5.5, 3.5 and 1.2 ng/g). In comparison, PCBs in sediments expressed in terms of these three Aroclor mixtures were in a 5 : 15 : 1 ratio. The bioaccumulation of penta- and hexachlorinated biphenyls predominant in Aroclor 1254 would be due to the metabolism of some of the less chlorinated PCBs and the greater bioavailability of these congeners relative to the more chlorinated ones [25-27]. Congeners 153, 138/163/164, 118, 187/182, 149 and 191 were more predominant in muscle tissue (Figure 4). This fingerprint indicates that hexachlorinated congeners 153 and 138 and pentachlorinated congener 118 have the highest tendency to bioaccumulate [26, 27]. Observed concentrations were all very low in muscle, where they displayed a distinct dose-response between E-0 and E-10, for congener 153 and 138/163/164, and an increase between E-0 and E-20 in sediments. Muscle of E-0 to E-10 flounder had similar lipid content (mean:0.7%, range: 0.5-0.8%), while muscle of E-20 flounder had a lower level (0.3%), possibly explaining the lack of dose-response for the higher level of exposure. Since most OC compounds were undetectable in sediments at the end of the four months exposure, few BSAF can be derived (Table 2).

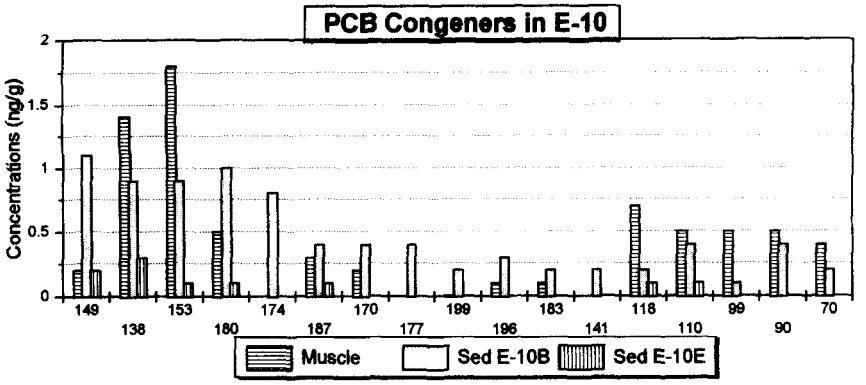


Figure 4. Polychlorinated biphenyl (PCB) congeners in muscle of finfish, sediments from the beginning (E-10B) and end (E-10E) of the exposure to 10% sludge in sediments.

Only naphthalene and C-1 naphthalene were detected in muscle, at a mean concentration of 5.3 and 2.3 ng/g, respectively (range: 3.9-6.7 and 1.4-2.8, respectively), but did not display a dose-response. The log K_{ow} of these low molecular weight PAHs indicates that equilibrium should be reached during the four months exposure. However, since in an earlier experiment higher concentrations were needed in sediments to determine bioaccumulation in the same species, it is suggested that metabolism takes place efficiently at the present lower concentrations [10].

The BSAF values in Table 2 range from 0.2 to 7, as would be expected by the equilibrium partitioning theory presented earlier, but lower BSAFs are likely when there is appreciable metabolism or equilibrium is slow. For example, in an exposure using the same finfish species under the same experimental conditions [12], using Hibernia crude oil instead of harbor sludge, a reasonably similar observed (0.03-12) to calculated (6.8) BSAF was obtained for PAHs with a log K_{ow} value below that of some methylphenanthrenes or methylanthracenes (log $K_{ow} \leq 5$, in [19]). Lower BSAF values of 0.1-0.01 were observed for fluoranthene, pyrene and chrysene (log K_{ow}= 5.22, 5.18 and 5.86, respectively; recommended in [19]). The latter larger molecular weight PAHs are less water soluble and more electronegative than the former and would be expected to take a longer time to reach equilibrium and undergo metabolism more readily than the smaller molecular weight PAHs. The time to reach equilibrium which depends on the respiration rate and lipid content of the finfish was

also discussed [12]. In the present case, compounds with log $K_{ow} \geq 6.5$ would take more than 4 months to equilibrate with the aqueous environment.

Bile metabolites

The presence of bile metabolites was also investigated after enzymatic hydrolysis. Only fish collected from the highest exposure displayed a measurable bioelimination of 1-hydroxypyrene, a PAH metabolite indicating exposure to combustion derived hydrocarbons. A very low mean concentration of 5 ng/μL corresponds to an exposure of 100 to 28 ng/g of pyrene in sediments from the beginning to the end of the exposure.

Assessment of the fate of priority contaminants derived from the harbor

Harbor sludge is a complex mixture of chemicals containing a wide variety of organic, inorganic and organometallic compounds of domestic and industrial origin, some well characterized and others more difficult to identify [e.g. 30-34]. Typically, sewage input can include household products, such as soaps, shampoos, cleaners, food additives and hospital and human derived chemicals and effluents from commercial and industrial sources. Contaminants present in road runoff include detritus, commonly used pesticides or herbicides on gardens and lawns and hydrocarbons deriving from fuels and combustion processes.

The present chemical analysis concentrated on a set of priority pollutants and one finfish species. It gave a partial view of the contaminants present in sludge and thus in harbor sediments. As observed elsewhere, biota living outside the harbor would also be exposed to a gradient of concentrations, since contaminants would be transported on colloidal and particulate matter [e.g. 6].

The levels of specific PAHs, total PAHs, total DDTs and total PCBs deduced for harbor sludge are above the "effect range low" proposed by the latest sediment quality guidelines, but below "effect range median" [35, 36]. The uptake of priority pollutants needs to be viewed in the actual context of this particular aquatic environment, where cumulative effects due to the poor water quality would be expected and explain the lack of biota in this harbor. It is hoped that this study will be of value in developing programs of contaminant monitoring and investigations in marine harbors which suffer poor water quality in part because of the continuing discharge of organic contaminants.

Acknowledgments:

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