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Geochemical Study of Sediment Contamination in New Bedford Harbor, Massachusetts

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ABSTRACT

Chemical analyses of sediment samples collected along a transect in New Bedford Harbor revealed a gradient of increasing concentrations of polychlorinated biphenyls (PCBs), polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), polycyclic aromatic hydrocarbons (PAHs) and several trace metals from the southern to the northern areas of the estuary. Although the concentrations of contaminants generally increased with distance north in the estuary for all classes of compounds, differences were observed between the trends for many of the compounds. These differences are probably due to both the sources and differential environmental behaviors of the compounds in the estuary. The primary sources of PCBs, PCDFs and trace metals appear to be industrial discharges either directly into the estuary or through combined sewer overflows. Additional inputs of PCDFs may have also impacted the lower portions of the harbor. These inputs may be from the combustion of sewage

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sludge containing high concentrations of PCBs at the New Bedford Harbor Municipal Wastewater Treatment Plant. The major inputs of PAHs and PCDDs are probably from urban runoff entering the harbor through combined sewer overflows and storm drains.

INTRODUCTION

The ecological health of many estuarine areas is threatened by the discharge of toxic compounds and the accumulation of these contaminants in sediments. The sediments of many industrialized estuaries contain high concentrations of anthropogenically produced or mobilized compounds (Bopp *et al.*, 1982; Pruell & Quinn, 1985; Schults *et al.*, 1987) and many of the contaminants found in estuarine sediments are biologically available (Rubinstein *et al.*, 1983; Pruell *et al.*, 1986). Thereby, sediment associated contaminants can affect biota or result in high concentrations in the tissues of indigenous organisms.

Contaminant sources to such areas are known to include sewage outfalls, industrial effluents, urban runoff, rivers and atmospheric deposition. A better understanding of the sources and environmental fates of contaminants is required to limit further degradation of urban estuaries and to remediate contaminated areas. Specifically, in New Bedford Harbor (NBH), detailed information on the spatial distribution of contaminants is required to determine how best to deal with this highly contaminated estuary, a portion of which has been designated an EPA Superfund Site (Weaver, 1984).

Several previous studies have shown that the sediments in some areas of NBH contain extremely high concentrations of PCBs and metals (Stoffers *et al.*, 1977; Weaver, 1984). The present study provides additional data on the geochemistry of PCBs and metals in the harbor as well as information on the concentrations and distributions of compounds from several chemical classes (PAHs, PCDDs and PCDFs) which, had not been previously studied in detail in NBH. These chemical data are used to produce a more complete geochemical picture of this estuary in order to gain a better understanding of the likely sources of contamination.

METHODS

Sediment collection

Sediments were collected from 12 locations in NBH (Fig. 1) on 21 and 22 January, 1986 using a Ponar grab sampler from the *R.V. East Passage*. A

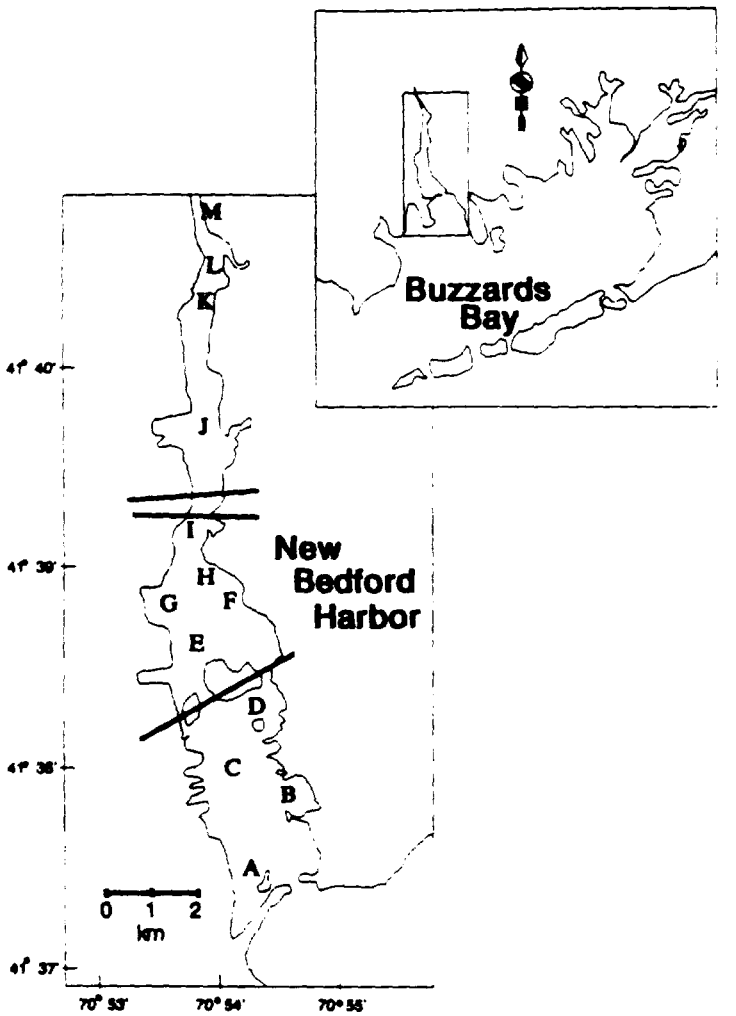

Fig. 1. Locations of sediment sampling stations in New Bedford Harbor.

sediment core (0–5 cm depth) was then taken from each of three grabs collected at a station. The contents of the cores (3·4 cm diameter polycarbonate core liners) from each station were combined and homogenized in cleaned glass jars. Sediment was collected from an additional site (Station M) on 6 January 1987. This sample was obtained in a shallow (5–10 cm water depth) area of the Acushnet River above the tidal influence of the estuary. Surface sediment (0–5 cm) was collected with a metal shovel, homogenized, and aliquots were placed into glass jars. All sediment samples were stored at 4°C prior to analysis.

The concentrations of total organic carbon (TOC), PCBs, PAHs and

several trace metals were measured in single sediment samples from each of the 13 stations. PCDDs and PCDFs were quantified in duplicate samples collected from stations B, J, L and M.

Total organic carbon

Samples to be analyzed for TOC were dried for 24 h at 100°C and then any shell fragments were removed. The sediment was ground to a fine powder and a portion weighed into a tin pan on a Cahn electrobalance (Model 4700). Carbon concentrations were measured using a Carlo Erba Model 1106 CHN analyzer.

Organic analysis

Sediment samples were thoroughly homogenized with a spatula and 1 to 10 g (wet weight) placed into a glass centrifuge tube. Recovery standards (octachloronaphthalene (OCN), phenanthrene-d_{10} and benz(a)anthracene-d_{12}) and 50 ml of acetonitrile were added. The samples were sonicated with an ultrasonic probe for 60 s then centrifuged at 10 000 rpm for 5 min in a refrigerated centrifuge at 4°C. The supernatant was decanted into a 1 liter separatory funnel containing 300 ml of deionized water and the extraction was repeated twice more and the extracts combined.

Fifty milliliters of pentane were added to the separatory funnel, the funnel was shaken, and the pentane layer removed. This was repeated twice more and the extracts combined and then dried with sodium sulfate. The pentane extract was reduced in volume using a heating mantle and a Kuderna-Danish evaporator with a 3-ball Snyder column, and the solvent exchanged to 1 ml of hexane.

The extracts were next fractionated using a 0·9 × 45 cm column which contained 11·5 g of BioSil A silicic acid (BioRad Laboratories) that had been fully activated, and then 7·5% deactivated with water. The first fraction (f_1) was eluted with 50 ml of pentane and a second fraction (f_2) was collected using 35 ml of 20% methylene chloride in pentane. The f_1 fraction was treated with activated copper powder to remove sulfur and then both fractions were reduced in volume as described above.

The f_1 fractions were analyzed for PCBs in three ways. These included (1) the traditional measure of PCBs as a manufactured formulation (e.g. Aroclor 1254), (2) quantitation of 12 individual PCB congeners and (3) by degree of chlorination using GC–MS.

For the Aroclor and congener analyses, 1 μl of each sample was injected in the splitless mode into a Hewlett–Packard 5840 gas chromatograph equipped with an electron capture detector and a 30-m DB5 fused silica

capillary column (J + W Scientific). Helium was the carrier gas at a flow rate of 1·5 ml/min and the flow of a 95:5 mixture of argon:methane to the detector was maintained at 35 ml/min. The oven temperature was held at 80°C for 4 min and then programmed from 80 to 290°C at 10°C/min. The injection port temperature was 270°C, and the detector was held at 300°C.

PCB concentrations in the extracts were measured as Aroclor 1254 by comparing peak heights in chromatograms of the sample extracts to those of quantitative Aroclor 1254 standards. Height measurements were made on seven prominent peaks in the sample chromatograms and the heights were summed. Solution concentrations were determined by comparing these sums to the same measurements made on standards of Aroclor 1254 that were analyzed at the beginning and end of each day. Sample concentrations were then calculated from sample dry weight data. The 12 congeners were quantitated against authentic standards using an external standard method.

The analytical procedures used for this study have been successfully intercalibrated with numerous laboratories (Galloway *et al.*, 1983). In addition, spike and recovery studies were conducted to determine the accuracy of the procedures. For these experiments a relatively uncontaminated sediment was spiked with numerous compounds. Recoveries averaged 71% for 2,4-dichlorobiphenyl, 80% for 3,3',4,4'-tetrachlorobiphenyl, 81% for 2,2',3,3',4,4',5,5'-octachlorobiphenyl, 71% for decachlorobiphenyl, and 71% for OCN. OCN was also spiked into each sample analyzed as part of this study and its recovery was measured. These recoveries averaged 86·6 ± 29·8% for all of the samples that were analyzed. Precision (relative standard deviation) of Aroclor 1254 measurements was determined by analyzing triplicate sediment samples. These determinations showed a relative standard deviation of 0·6%.

PCBs were also quantitated by degree of chlorination using gas chromatography–mass spectrometry (GC–MS). These analyses and PAH quantitations (f_2 fraction) were conducted using a Finnigan 4531 GC–MS with a CDC 96 megabyte drive and a Nova 3 computer running INCOS software. The GC was operated in the splitless injection mode and contained a 30-m DB5 fused silica capillary column. The GC oven was held at an initial temperature of 50°C for 2 min, programmed to 330°C at 10°C/min and held at that temperature for an additional 9 min. The instrument was operated in the electron-impact mode at 70 electron volts and 300 microamperes. The various source potentials were adjusted to produce a spectrum of decaflurotriphenylphosphine (DFTPP) which met the specifications detailed by Eichelberger *et al.* (1975).

PCB measurements by chlorine number were made using GC–MS software routines developed by Slivon *et al.* (1985) and Total PCB concentrations were calculated by summing the values for each level of

chlorination. For these quantitations, an internal injection standard (chrysene-d_{12}) was added to each extract just prior to analysis. Also, to determine response factors, a standard solution containing the internal injection standard and Aroclor 1254 was analyzed at the beginning and end of each day. PAH quantitations were accomplished using two internal standards, phenanthrene-d_{10} and benz(a)anthracene-d_{12}, which were spiked into samples just before extraction. GC–MS identifications were made using retention times and extracted ion current profiles (EICPs). Spectra were checked if unusual peak patterns were observed. Quantitations were made using the EICPs of the internal standards and the compounds of interest. The recovery of PAHs through the analytical procedure was $60 \pm 7\%$.

A reagent blank was analyzed along with each set of six samples. The compounds of interest were not found in significant amounts in any of the blanks.

The analysis procedures used for the PCDDs and PCDFs were similar to those described by Kuehl *et al.* (1987). Briefly, the sediment samples were dried, and Soxhlet extracted with benzene. The extract was volume reduced and solvent exchanged to isooctane. The sample was then passed through a column containing sodium sulfate and separate layers of silica gel that were treated with sulfuric acid and potassium hydroxide. The extracts were also purified up using alumina, silver ion silica gel and a silica gel/carbon column (Amoco PX-21). Identifications and quantitations were conducted on a Finnigan-MAT 8230 double focusing GC-MS. Samples were chromatographed on both 30-m DB5 and 60-m SP2330 (Supelco, Inc.) columns. Carbon-13-labelled internal standards for each isomer group were used for quantitations.

Inorganic analysis

Sediments were homogenized by hand-stirring with a spatula and then approximately 5 g of wet sediment were transferred to acid-cleaned, polyethylene bottles. Also, separate subsamples were taken for wet-to-dry weight ratio determinations. The samples were acidified with 50 ml of 2N HNO_3, sealed with polyethylene screw caps, and immersed in an ultrasonic water bath at ambient temperature for 6 h. After standing overnight, the samples were filtered through acid-washed (2N HNO_3) Whatman 41 filter paper into 60 ml, acid-cleaned, polyethylene bottles.

Flame atomization–atomic absorption spectrophotometry (FA–AAS) was conducted on the samples with a Perkin–Elmer (Model 5000) AAS. FA–AAS signals were recorded with a Perkin–Elmer strip chart recorder (Model 56) and the absorbance data processed by a Perkin–Elmer Model 3600 data station microcomputer. Calibration curves generated by poly-

nomial regression of absorbance data for standards were used to determine concentrations.

The instrument conditions for FA-AAS determinations were similar to those described in '*Methods for Chemical Analysis of Water and Wastes*' (US EPA, 1979) and in the manufacturer's reference manuals. The AA instrument was calibrated each time samples were analyzed for a given element and calibrations were generally checked after every fifth sample. Samples were analyzed at least twice to determine signal reproducibility. A blank sample was analyzed for each set of about 15 samples. For each element (except iron), two samples from each set were also analyzed by the method of standard additions. All blanks were below instrumental detection limits. Spike recoveries were 97 ± 9% for chromium, 103 ± 1% for copper, 104 ± 5% for zinc, 104 ± 1% for cadmium, 107 ± 3% for lead, 103 ± 2% for nickel, and 106 ± 2% for manganese. In addition, standard reference sediments from our laboratory were analyzed with each set of samples.

RESULTS AND DISCUSSION

Total organic carbon

The concentrations of TOC in the sediment increased from 29 to 120 mg/g from Stations A to L then decreased to 32 mg/g at Station M (Table 1). At Stations A, B and M the concentrations measured were similar to those previously reported for the relatively uncontaminated lower portion of Narragansett Bay, Rhode Island (Pruell & Quinn, 1985) and from a reference site in Long Island Sound (Munns *et al.*, 1989). At Stations J, K and L, the respective amounts of organic carbon in the sediments were 98·2, 110 and 121 mg/g. These concentrations are higher than have previously been reported in Southern New England estuaries.

PCBs

Changes were seen in both the concentrations and distributions of PCB congeners throughout the harbor. The total PCB concentrations increased from 6·1 to 2100 μg/g (a factor of about 340) between Stations A and L (Table 1). Concentrations measured as Aroclor 1254 ranged from 3·8 to 540 μg/g between Stations A and L (a factor of 140) then decreased to 4·1 μg/g at Station M (Table 1). The ratio of Aroclor 1254 to total PCBs was variable and ranged from 0·41–0·69 with a mean of 0·53 for Stations A–J. This ratio was lower at Stations K and L (0·36 and 0·26, respectively). The

TABLE 1
TOC and PCB Concentrations as Aroclor 1254 and Total PCBs in Sediments Collected Along a Transect in New Bedford Harbor

Station	*TOC* (*mg g dry wt*)	*Aroclor 1254* (*μg g dry wt*)	*Total PCBs*[a] (*μg g dry wt*)	*1254 Total ratio*
A	29·0	3·9	9·4	0·41
B	36·0	3·8	6·1	0·62
C	47·0	5·1	11·0	0·46
D	47·0	5·5	8·0	0·69
E	57·0	11·0	18·0	0·61
F	71·0	19·0	47·0	0·40
G	55·0	14·0	32·0	0·44
H	58·0	14·0	21·0	0·67
I	42·0	14·0	30·0	0·47
J	98·0	150	300	0·50
K	110·0	310	850	0·36
L	120·0	540	2 100	0·26
M	32·0	4·10	na	na

[a] Total PCBs calculated by summing the GCMS values for each level of chlorination.
na—Not analyzed.

same trend can be seen in the degree of chlorination data (Fig. 2a). The patterns were very similar in samples collected from Stations A–I; therefore, the data from these locations were averaged for Fig. 2a. Compounds containing four and five chlorines were in highest concentrations in samples from these stations. A change occurred in the PCB distribution at Station J which became more pronounced at Stations K and L. In these samples compounds containing three and four chlorine atoms were found in the highest relative proportions. The relative amounts of dichlorobiphenyls also increased greatly at these locations.

This increase in the concentrations and proportions of lower molecular weight PCBs at stations further north in the estuary can also be seen in the individual congener data (Table 2). The two tetrachlorobiphenyls that were quantified (047 and 052) increased in concentration from Station A to L by more than a factor of 500. The largest increase seen along the transect for any of the more chlorinated compounds was less than a factor of 200.

Comparisons of the sediment plots in Fig. 2a with those of the Aroclors (Fig. 2b) indicate that the sediments contain mixtures of Aroclors. NBH sediments contain PCBs that appear to be mixtures of Aroclors 1016 and/or 1242 and Aroclor 1254. However, it is not possible to differentiate between 1016 and 1242 in NBH sediments because these formulations are very

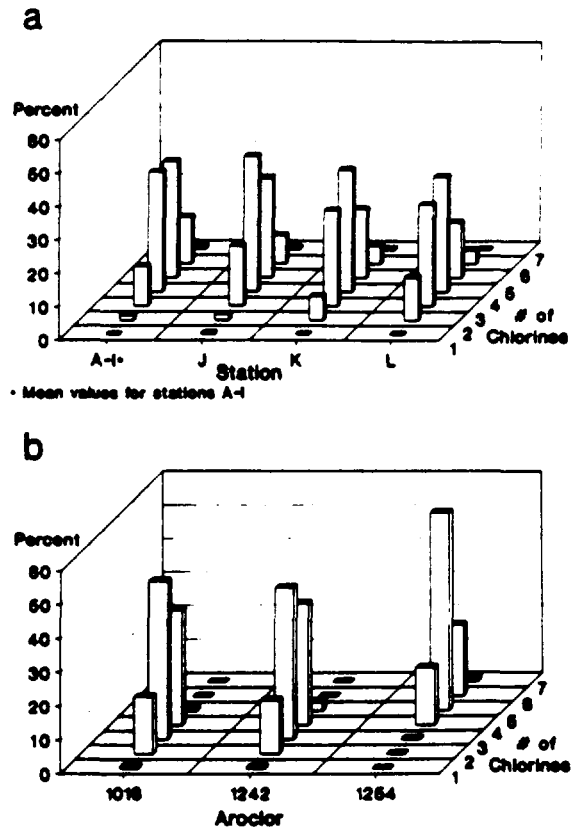

Fig. 2. Percent abundance of PCBs for each degree of chlorination in (a) New Bedford Harbor sediments and (b) Aroclors 1016, 1242 and 1254.

similar except in the portion of the chromatogram influenced by Aroclor 1254.

The major inputs of PCBs to NBH are believed to have come from a factory located just north of Station L. The two stations just south of this location (K and L) contain the highest concentrations of PCBs and the largest relative amount of the lower chlorinated congeners. Samples from all of the stations south of Station J show PCB distributions that are similar to each other and do not contain the relatively high proportions of lower chlorinated compounds.

Several reasons could account for the changes seen in the mixtures of PCBs within the harbor. First, PCB-contaminated sediment may be resuspended in the upper areas of the bay and then transported downbay. During this process the less chlorinated congeners, which have greater water solubilities, may be preferentially lost to the dissolved phase. Therefore, the particles that settle in the lower portion of the bay may be proportionally

TABLE 2
Concentrations of Individual PCB Congeners in Sediments Collected from New Bedford Harbor

Station	*PCB[a] Congener (μg/g dry wt)*											
	052	*047*	*101*	*151*	*118*	*153*	*138*	*128*	*180*	*194*	*206*	*209*
A	0·32	0·14	0·43	0·90	0·53	0·35	0·35	0·13	0·058	0·011	0·006	0·004
B	0·17	0·097	0·29	0·56	0·40	0·26	0·26	0·092	0·045	0·009	0·005	0·002
C	0·20	0·097	0·30	0·061	0·38	0·26	0·26	0·090	0·042	0·007	0·004	0·003
D	0·44	0·23	0·64	0·15	0·78	0·53	0·56	0·21	0·099	0·018	0·009	0·005
E	0·77	0·44	1·3	0·26	1·7	1·2	1·1	0·39	0·21	0·041	0·025	0·016
F	1·9	0·93	3·0	0·68	3·6	2·3	2·7	1·0	0·51	0·096	0·057	0·030
G	1·4	0·81	2·1	0·40	2·6	1·7	1·7	0·60	0·32	0·063	0·035	0·020
H	1·4	0·82	1·9	0·37	2·3	1·5	1·4	0·50	0·27	0·053	0·032	0·018
I	1·3	0·84	1·8	0·34	2·2	1·5	1·3	0·45	0·26	0·051	0·031	0·016
J	12·0	7·0	14·0	2·3	15·0	9·1	6·6	2·3	1·4	0·28	0·17	0·084
K	51·0	25·0	36·0	5·5	28·0	22·0	13·0	3·9	2·9	0·65	0·41	0·15
L	170·0	73·0	79·0	11·0	70·0	54·0	26·0	6·8	5·7	0·13	0·86	0·38
M	0·32	0·13	0·17	0·048	0·16	0·11	0·13	0·043	0·025	0·005	0·55	0·003

[a] PCB Identifications (Ballschmiter & Zell, 1980):

052—2,2′,5,5′-TCB
047—2,2′,4,4′-TCB
101—2,2′,4,5,5′-PeCb
151—2,2′,3,5,5′,6-HxCB
118—2,3′,4,4′,5-PeCB
153—2,2′,4,4′,5,5′-HxCB
138—2,2′,3,4,4′,5′-HxCB
128—2,2′,3,3′,4,4′-HxCB
180—2,2′,3,4,4′,5,5′-HpCB
194—2,2′,3,3′,4,4′,5,5′-OCB
206—2,2′,3,3′,4,4′,5,5′,6-NCB
209—2,2′,3,3′,4,4′,5,5′,6,6′-DCB.

depleted in the lower chlorinated PCBs compared with sediments from the northern portion of the harbor.

Another explanation for the observed distributions may be differential inputs in combination with changes in sediment deposition rates along the gradient. Company records indicate that several different Aroclor mixtures were used by the factories bordering NBH. The records show that Aroclors 1254, 1242 and 1016 were the predominant PCB formulations used and that Aroclor 1254 was used prior to the use of Aroclors 1242 and 1016 (C. Bering, US EPA-Region I, pers. comm.). Therefore, the relative distributions of these PCB formulations with depth in the sediments could be different. Surface sediment would be expected to be enriched in Aroclor 1016/1242, while deeper sediment may contain more Aroclor 1254. Brownawell & Farrington (1986) observed this trend in a sediment core taken from outer New Bedford Harbor.

Summerhayes *et al.* (1977) reported that the silt deposits in the harbor are deepest above the New Bedford–Fairhaven Bridge and that the sedimentation rate is higher in the northern areas of the harbor. Therefore, samples which were collected at constant depth horizons may represent different depositional intervals. Since the samples collected for the present study included the top 5 cm of sediment at all stations, in areas of rapid net sedimentation (e.g. 1 cm/year) this sample could represent material deposited over the last 5 years. Whereas, in an area with a net sedimentation rate of 0·2 cm/year, 5 cm of sediment may include material deposited over the past 25 years. Because of this, the surface sediments of the upbay sites could contain mostly Aroclor 1016/1242; whereas areas with low net sedimentation rates may show greater relative amounts of Aroclor 1254 near the sediment surface.

A third possibility is that changes in PCB congener patterns within the harbor could result from differences in bioturbation rates or depths at various locations within the estuary. The sediments of heavily contaminated areas often have very shallow bioturbation zones because of impacts on the biota due to toxicity or low oxygen concentrations. Therefore, the historical record of inputs may be well preserved in the sediments of such areas. Less contaminated sediments with more active biological communities often show a poorly defined historical record of inputs. Pruell & Quinn (1985) reported a well preserved record of inputs in sediments from the contaminated upper portion of Narragansett Bay and a smeared record of inputs further downbay in less contaminated areas. A similar occurrence in NBH could produce a distinct layer containing mostly Aroclor 1016/1242 in the surface of the cores from the northern areas of the estuary. Bioturbation of sediments in the lower harbor would tend to mix Aroclor 1254 from deeper in the sediment with the more recent releases of Aroclor 1016/1242.

Because of this process, the surface sediments in the lower harbor may contain proportionally greater amounts of Aroclor 1254 when compared with those from upper harbor locations.

It has recently been reported that anaerobic dechlorination of PCBs is occurring in heavily PCB contaminated sediments from some locations including NBH (Brown *et al.*, 1987). The congener profiles seen in the surface samples from the present study are not consistent with dechlorination as an explanation for the lower molecular weight congener distributions in the northern portion of the estuary. However, more recent work on sediment core sections from heavily contaminated areas of NBH has revealed congener profiles that are consistent with anaerobic dechlorination (J. L. Lake, US EPA-Narragansett, pers. comm.).

PCB concentrations up to 2100 μg/g were measured in the sediments of NBH in the present study and much higher concentrations have been reported in sediments from different sites in the harbor by other investigators (Weaver, 1984). These concentrations are higher than have been found in other New England estuarine sediments which generally contain less than 10 μg/g of PCBs (Boehm *et al.*, 1984; Pruell *et al.*, 1986; Gardner & Pruell, 1987; Munns *et al.*, 1989). The highest PCB concentration in sediments measured as part of the NOAA Status and Trends Program (NOAA, 1987) was 17·1 μg/g for Boston Harbor. In fact, the PCB concentrations in the sediments of NBH are higher than have been reported for any other estuary including the Hudson River (Bopp *et al.*, 1982).

PCDDs and PCDFs

Much recent attention has been focused on PCDDs and PCDFs as environmental contaminants because of their extreme toxicity, bioaccumulation potential and widespread distribution. However, very few studies have investigated the occurrence of these compounds in the marine environment. In the present study several PCDDs and PCDFs were measured in sediments collected from four sites (Stations B, J, L and M) along the transect in NBH.

PCDD concentrations were generally lowest at Stations B and M (Table 3). Compounds containing four, five or six chlorines were near or below the analytical detection limits in these samples; however, measurable concentrations of 1,2,3,4,6,7,8-heptachlorodibenzo-*p*-dioxin and octachlorodibenzo-*p*-dioxin (OCDD) were found. Slightly higher PCDD concentrations were found in samples from Stations J and L. The highly toxic congener, 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (2,3,7,8-TCDD), was only detected (detection limit of about 1 pg/g) at station L (4·4 pg/g). Tiernan (1986) measured the concentrations of PCDDs in three sediment samples from NBH. That study

TABLE 3
Average Concentrations for Duplicate Analyses of Selected Polychlorinated Dibenzo-*p*-Dioxins in New Bedford Harbor Sediments

Station	*PCDD[a] Congener (pg/g dry weight)*						*Total*
	48	*54*	*67*	*70*	*73*	*75*	
B	nd	nd	24·0	19·0	1 100	4 000	5 100
J	nd	21·0[b]	69·0	54·0	910[b]	7 000	8 100
L	4·4	25·0	110	70·0	1 100	5 800	7 100
M	nd	nd	32·0	nd	300	1 400	1 700

[a] PCDD Identifications (Ballschmiter *et al.*, 1986):
48—2,3,7,8-TCDD
54—1,2,3,7,8-PeCDD
67—1,2,3,6,7,8-HxCDD
70—1,2,3,7,8,9-HxCDD
73—1,2,3,4,6,7,8-HpCDD
75—1,2,3,4,5,6,7,8-OCDD.
[b] Detected in one of two samples.
nd—Not detected, detection limits ranged from about 1–10 pg g^{-1} depending on the congener and sample.

did not detect 2,3,7,8-TCDD but found some of the more chlorinated PCDD congeners in concentrations similar to those measured in the present study.

Norwood *et al.* (1989) compared the concentrations of 2,3,7,8-TCDD and 1,2,3,7,8-pentachlorodibenzo-*p*-dioxin in the sediments of several New England estuaries. Samples from Black Rock Harbor, Connecticut, and Narragansett Bay contained higher concentrations than those measured in NBH. Concentrations of 2,3,7,8-TCDD found in sediments from three locations in the Hudson River (O'Keefe *et al.*, 1984) ranged from $<5{\cdot}6$ to 10 pg/g with the highest concentrations being found in the lower portion of the river. Much larger amounts of 2,3,7,8-TCDD have been found in sediments from the Passaic River, New Jersey (Belton *et al.*, 1985) near a chemical plant that manufactured 2,4,5-trichlorophenoxyacetic acid. The sediments of the Passaic River contained 2,3,7,8-TCDD concentrations as high as 6900 pg/g.

Several PCDF congeners were also measured in the sediments from Stations B, J, L and M (Table 4). The concentrations of these compounds generally increased with distance north from Stations B to L then decreased at Station M. In addition to the concentration changes, there were also major differences in the congener and isomer ratios in the samples. In particular, several of the PCDFs containing 4–6 chlorines showed considerably elevated concentrations relative to compounds containing

TABLE 4

Average Concentrations for Duplicate Analyses of Selected Polychlorinated Dibenzofurans in New Bedford Harbor Sediments

Station	*PCDF[a] Congener (pg/g dry weight)*													*Total*
	81	*83*	*86*	*94*	*112*	*114*	*115*	*118*	*121*	*130*	*131*	*134*	*135*	
B	290	740	37·0[b]	350	37·0	70·0	31·0	32·0[b]	22·0[b]	7·0	280	nd	220	2 100
J	1 100	1 410	280	410	150[b]	300	260	310	190	42·0	720	170	630	6 000
L	900	1 180	280	500	160	580	450	1 400	770	120	1 200	290	1 200	9 000
M	6·0	10.0	2·0[b]	nd	nd	nd	62·0	17·0[b]	nd	nd	120	26·0[b]	170	140

[a] PCDF Identifications (Ballschmiter *et al.*, 1986):

81 2,3,6,7-TCDF
83—2,3,7,8-TCDF
86—3,4,6,7-TCDF
94—1,2,3,7,8-PeCDF
112—2,3,4,6,7-PeCDF
114—2,3,4,7,8-PeCDF
115—1,2,3,4,6,7-HxCDF
118—1,2,3,4,7,8-HxCDF
121—1,2,3,6,7,8-HxCDF
130—2,3,4,6,7,8-HxCDF
131—1,2,3,4,6,7,8-HpCDF
134—1,2,3,4,7,8,9-HpCDF
135—1,2,3,4,5,6,7,8-OCDF.

[b] Detected in one of two samples.

nd—Not detected, detection limits ranged from about 1–10 pg g^{-1} depending on the congener and sample.

seven and eight chlorines in the samples from Stations B, J and L when compared with those from Station M. However, unlike the PCBs which showed relatively enriched amounts of the lesser chlorinated congeners at Station K and L relative to the lower harbor sites, there was little difference in the PCDF ratios in the samples from Stations B, J and L.

Norwood *et al.* (1989) used principal components analysis to compare the NBH, PCDD and PCDF data from the present study with data from several other coastal New England locations. In this analysis, the NBH Station M results (Table 4) grouped with results from a relatively uncontaminated site in Central Long Island Sound. This may represent background concentrations resulting from long distance atmospheric transport and deposition (Czuczwa & Hites, 1984). The PCDF concentrations measured at Stations B, J and L in NBH were all well above those found at the other New England coastal locations and grouped separately (Norwood *et al.*, 1989). The congeners containing four or five chlorines, which are the most toxic compounds (Safe, 1987), were elevated to a greater extent than were the more chlorinated compounds.

Tiernan (1986) measured 2,3,7, 8-tetrachlorodibenzofuran (2,3,7,8-TCDF) concentrations ranging from 406-730 pg/g in sediments from three stations in NBH. These are somewhat lower than the concentrations found in the present study (740–1410 pg/g); however, it is difficult to directly compare the results because exact station locations are not provided. Much lower 2,3,7,8-TCDF concentrations (5–46 pg/g) were reported in sediments from the Hudson River (O'Keefe *et al.*, 1984).

PAHs

Numerous PAHs were also quantitated in the NBH sediment samples. The concentrations of some of the more abundant compounds and total PAH concentrations are presented in Table 5. The relative distributions of PAH compounds were similar at all of the stations. The most abundant compounds included phenanthrene, fluoranthene, pyrene, benz[a]anthracene, chrysene and benzo[a]pyrene. This pattern, dominated by parent compounds with lesser amounts of the alkylated homologs, mimics those found worldwide in marine sediments (Laflamme & Hites, 1978; Lake *et al.*, 1979). The major sources of these compounds are combustion processes.

The concentrations of PAHs in the sediments of NBH, particularly the northern portion of the estuary (Stations J, K and L), are very high relative to those found in sediments remote to urban areas (Laflamme & Hites, 1978; Larsen *et al.*, 1986). However, concentrations measured in NBH are similar to those measured in other northeastern urban estuaries including Black Rock Harbor (Rogerson *et al.*, 1985), Narragansett Bay (Lake et al., 1979;

TABLE 5
Concentrations of PAHs in Sediments Collected from New Bedford Harbor

Station	*PAH* Compound (μg/g dry weight)*											
	FL	*PHEN*	*ANTH*	*FLUO*	*PYR*	*B[a]A*	*CHRY*	*B[a]P*	*IND*	*B[ghi]P*	*D[a,h]A*	*Total*
A	0·09	0·90	0·34	1·8	2·2	0·96	1·2	1·1	0·72	0·74	0·23	19·0
B	0·06	0·45	0·21	1·4	1·7	0·64	0·82	0·84	0·55	0·58	0·18	14·0
C	0·06	0·61	0·35	1·9	2·4	1·1	1·4	1·3	0·81	0·84	0·24	22·0
D	0·07	0·70	0·20	1·3	2·0	0·90	1·2	1·4	0·90	0·94	0·33	20·0
E	0·16	0·87	0·25	3·5	3·5	1·5	2·00	1·8	1·2	1·2	0·40	34·0
F	0·051	0·49	0·074	1·4	1·6	0·65	0·91	1·1	0·81	0·87	0·27	18·0
G	0·12	1·3	0·31	2·6	3·3	1·2	1·6	1·7	1·2	1·3	0·42	30·0
H	0·15	1·5	0·36	3·2	3·5	1·6	2·1	2·0	1·4	1·4	0·50	35·0
I	0·11	1·2	0·26	2·5	2·8	1·2	1·4	1·5	1·1	1·1	0·34	26·0
J	1·6	17·0	4·7	21·0	19·0	8·4	8·7	8·4	5·4	5·4	1·9	170·0
K	0·44	4·8	0·86	8·5	8·4	3·8	4·4	4·4	3·2	3·3	1·1	81·0
L	0·55	5·6	1·5	16·0	14·0	5·6	6·6	6·4	4·9	4·8	1·7	130·0
M	0·15	3·0	0·52	4·8	4·0	1·7	2·0	1·8	1·2	1·3	0·37	34·0

* PAH Identifications:

FL—Fluorene
PHEN—Phenanthrene
ANTH—Anthracene
FLUO—Fluoranthene
PYR—Pyrene
B[a]A—Benz[a]anthracene
CHRY—Chrysene
B[a]P—Benzo[a]pyrene
IND—Indeno[1,2,3-cd]pyrene
B[ghi]P—Benzo[g,h,i]perylene
D[ah]A—Dibenz[a,h]anthracene
Total—This also includes C1-C4 PHENs/ANTHs, benzfluoranthenes, perylene, coronene and all mw 276, 278 and 302 PAHs.

Pruell & Quinn, 1985) and Quincy Bay, Massachusetts (Gardner & Pruell, 1987).

Metals

Three different trends were observed for metal concentrations in the sediments of the harbor (Table 6). Cadmium, copper, chromium and nickel concentrations increased from Station A to J then decreased at Stations K, L and M. For lead and zinc the concentrations maximized at Station L while iron and manganese remained relatively uniform throughout the harbor.

The Massachusetts Division of Water Pollution Control (MDWPC) measured copper, chromium and nickel concentrations of 7250, 3200 and 550 $\mu g\,g^{-1}$, respectively, at a station about 1·8 km south of our Station J (Summerhayes *et al.*, 1977). The concentrations that we found at Station J (2500, 1700 and 210, respectively) were somewhat lower. Both studies found that the cadmium concentrations were highest near Station J with MDWPC reporting 76 $\mu g\,g^{-1}$ of cadmium, which is almost identical to our value of 78·0 $\mu g\,g^{-1}$. The lead and zinc concentrations measured in the present study at Station J were 610 and 2200, respectively, which also compare well with 560 $\mu g\,g^{-1}$ for lead and 2300 $\mu g\,g^{-1}$ for zinc reported by MDWPC. Summerhayes *et al.* (1977) and Stoffers *et al.* (1977) reported metals concentrations in the clay fractions of a sediment core collected near Station J and reported results very similar to those of the

TABLE 6
Concentrations of Selected Metals in Sediments Collected from New Bedford Harbor

Station	*Metal (µg/g dry weight)*							
	Cd	*Cu*	*Cr*	*Ni*	*Pb*	*Zn*	*Mn*	*Fe*
A	4·1	370	180	19·0	120	260	99·0	12 000
B	4·4	440	180	27·0	150	390	120	16 000
C	3·8	470	210	23·0	150	330	140	17 000
D	4·3	650	340	24·0	170	330	140	17 000
E	5·8	890	420	39·0	250	520	170	23 000
F	6·1	1 800	940	36·0	520	490	160	22 000
G	8·0	1 500	770	33·0	260	560	100	14 000
H	10·0	1 500	750	46·0	290	660	130	18 000
I	7·9	930	470	51·0	240	580	110	14 000
J	78·0	2 500	1 700	210	610	2 200	140	19 000
K	70·0	1 500	1 100	140	730	2 400	160	17 000
L	47·0	1 200	710	140	880	2 500	160	17 000
M	<0·3	20·0	6·7	5·1	230	69·0	69·0	10 000

present study; however, detailed comparisons may not be appropriate because of the different sample types.

The concentrations of cadmium, copper, chromium, nickel, lead and zinc in the sediments of the northern portion of NBH are generally much higher than those reported in other estuarine areas. Lead concentrations were higher than those measured in Long Island Sound sediments (Greig *et al.*, 1977) by at least a factor of 4 and cadmium was enriched by about a factor of 19. All of the copper concentrations measured throughout NBH were higher than those reported for Long Island Sound (Greig *et al.*, 1977). NBH metals concentrations exceeded Narragansett Bay (Oviatt *et al.*, 1984) and Quincy Bay (Gardner & Pruell, 1987) concentrations by factors of 50–60 for cadmium, 10–20 for copper and 5–6 for lead. Similarly, concentrations of cadmium, copper, chromium and lead reported by the National Status and Trends Program (NOAA, 1987) for sediments taken from along the United States coastline were all less than those measured in the northern portion of NBH in the present study, except for chromium in Salem Harbor, MA. The NBH trace metal concentrations, however, are similar to those of Black Rock Harbor (Rogerson *et al.*, 1985). Very similar concentrations of copper, chromium, and nickel were seen in these two sediments. Concentrations of cadmium, lead and zinc were 2–3 times higher in sediments from NBH than those from Black Rock Harbor.

No trends were observed along the transect for manganese and iron concentrations in the present study. MDWPC reported similar results for manganese, but found changes in the iron concentrations in different areas of the estuary.

Sources

In general, the concentrations of all contaminants and TOC increase with distance north in the NBH estuary (Fig. 3). The trends, however, were not the same for all of the classes of compounds or even for some of the compounds within chemical classes. This indicates that there are differences in the sources of the contaminants and/or their geochemical behaviors differ.

Our data suggest that the major source of PCBs to NBH was located in the northern portion of the estuary near our Station L. Total PCB concentrations were highest at this site and decreased rapidly with distance downbay (Fig. 3a). Station L is located very close to a factory which manufactured electrical equipment and is suspected of being responsible for much of the PCB contamination within the estuary.

Some of the PCDDs and PCDFs measured in the sediments of the harbor are the result of long distance atmospheric transport of these compounds (Czuczwa & Hites, 1984). The magnitude of this source is probably reflected

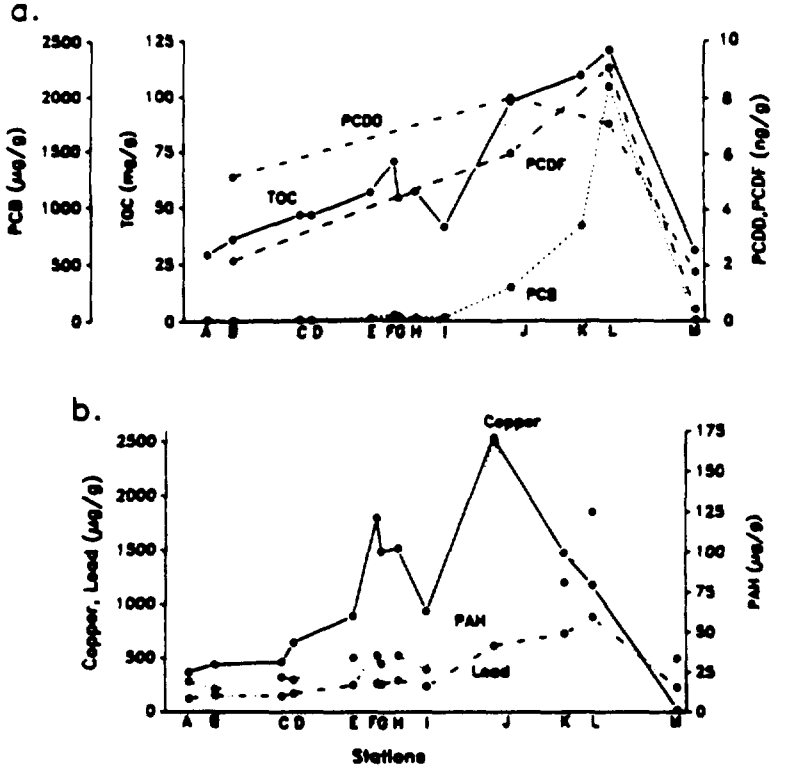

Fig. 3. Concentrations of (a) TOC, total PCBs, total PCDDs, total PCDFs, (b) total PAHs, copper and lead in sediments collected along a south to north transect of New Bedford Harbor.

by the concentrations measured at Station M. Since the concentrations of these compounds in the remainder of the harbor are much higher, additional sources are likely. The trends for total PCDDs and PCDFs were somewhat different (Fig. 3a). Since these compounds are probably similar geochemically, the major sources of the PCDDs and PCDFs may be different.

There has been considerable debate in the literature over the sources of PCDD and PCDF compounds in the environment (Hutzinger *et al.*, 1985). Potential sources for these compounds include various chemical manufacturing processes and incomplete combustion. Many studies have shown that PCDDs and PCDFs are produced in municipal incinerators (Buser *et al.*, 1978; Czuczwa & Hites, 1984). Also, recent work (Marklund *et al.*, 1987) indicates that automobiles burning leaded gasoline may be major sources of these compounds.

Since PCDFs are contaminants in commercial PCB mixtures (Albro & Parker, 1979; Cull & Dobbs, 1984; Wakimoto *et al.*, 1988), large amounts of

PCDFs may have been released to NBH along with the PCBs. However, the concentrations of PCDFs in the sediments of NBH are considerably higher than would be expected based on PCB concentrations. This is especially true for tetrachlorodibenzofurans and pentachlorodibenzofurans in the southern portion of the estuary. For example, the concentration of 2,3,7,8-TCDF at Station B is 880 times higher (Fig. 4a) than expected based on the amount of PCBs present and 2,3,7,8-TCDF concentrations of PCB mixtures (Wakimoto *et al.*, 1988).

The PCB concentration in sediment from Station L is more than a factor of 300 higher than that at Station B (Table 1), yet the concentrations of

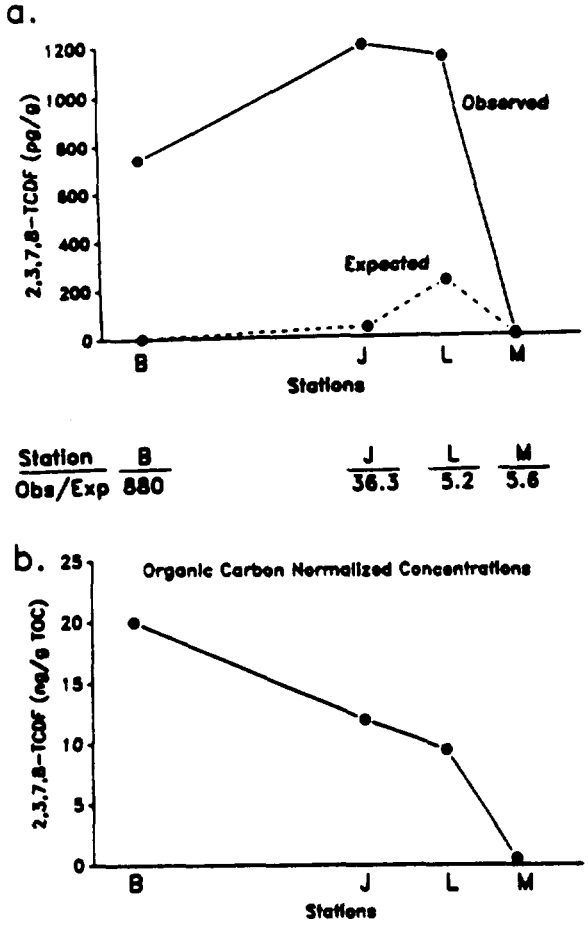

Fig. 4. (a) Observed and expected concentrations of 2,3,7,8-TCDF calculated from 2,3,7,8-TCDF concentrations in Aroclor mixtures (Wakimoto *et al.*, 1988) and sediment PCB concentrations. (b) TOC normalized concentrations of 2,3,7,8-TCDF in New Bedford Harbor sediments.

2,3,7,8-TCDF measured at these two locations differ by less than a factor of 2 (Table 4). This change in the ratios of PCBs and PCDFs could be caused by differences in the behavior of the compounds or as the result of additional sources of PCDFs in the lower portion of the harbor. PCBs and PCDFs are both relatively stable compounds with very similar solubilities and partition coefficients (Burkhard & Kuehl, 1986); therefore, it is unlikely that the observed distributions are due to the differential movement of these compounds in the estuary. Instead, there may be an additional source of PCDFs to the lower harbor area.

Large amounts of PCBs are known to have been released into the sewage system of New Bedford and high PCB concentrations were reported in sludge from the New Bedford Municipal Wastewater Treatment Plant (Weaver, 1982). This facility burned its sludge in an onsite incinerator. Since PCDFs have been shown to be formed during the combustion of PCBs (Addis, 1986; des Rosiers, 1987), one possible source of PCDFs may be the incineration of PCB-contaminated sewage sludge at the sewage treatment plant which is located about 10 km south of Station B. PCDFs may have been released to the atmosphere from this operation and significant amounts may have contaminated the lower harbor due to atmospheric fallout. Other undocumented sources of these compounds may have also contributed.

The biological availability of sediment bound contaminants to aquatic organisms is presently not completely understood. However, for nonpolar organic chemicals, the organic carbon content of the sediment is a major factor controlling the available concentrations (Lake *et al.*, 1987). Because of this, contaminant concentrations are often normalized to TOC. When 2,3,7,8-TCDF concentrations in NBH are normalized to TOC (Fig. 4b), the results indicate that the biologically available amounts of this compound may be highest in the southern areas of the estuary. This is because TOC concentrations increase to a greater extent than do PCDFs with distance north in the estuary.

The total PAH and total PCDD concentrations are highest at Station J (Fig. 3a and 3b) which is close to where several combined sewer overflows (CSOs) empty into the harbor. The CSOs are probably the major sources of these compounds. Cadmium, copper, chromium and lead concentrations are highest at Station J and these CSOs may contribute to this contamination (Fig. 3b and Table 6). However, the major source of metals is believed to be an industrial discharge located about 2 km south of this area (Stoffers *et al.*, 1977). The spatial distributions of lead and zinc are different from the other trace metals (Fig. 3b and Table 6). These elements increase in concentration with distance north all the way to Station L and show strong correlations with TOC. Therefore, these metals may behave differently from the others

once released to the harbor or there may have been major releases of lead and zinc near Station L.

In summary, NBH has received large inputs of chemical contaminants from many sources, and because of these inputs, its sediments are contaminated with a complex mixture of toxic compounds. The concentrations of contaminants in NBH equal or exceed those of other industrialized harbors in the United States. Spatial distributions suggest multiple sources for the contamination. Because the distributions of contaminants are complex, remediation of excessive concentrations of PCBs in the Superfund site should also consider the environmental implications of contaminants that do not covary distributionally with PCBs and the joint effects of all contaminants associated with sediments from the harbor. In addition, in order to prevent the further deterioration of near coastal areas, more work is needed to better define the sources of these contaminants so that the major sources can be identified and controlled.

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