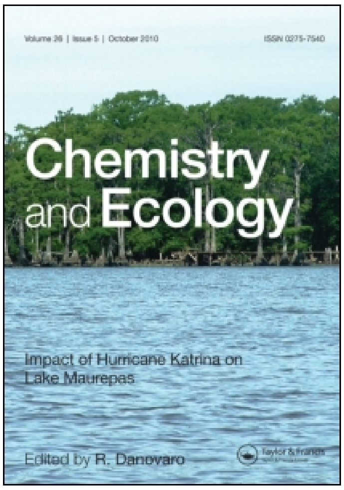

Chemistry and Ecology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455114

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To cite this Article Roethel, Frank J. and Breslin, Vincent T.(1995) 'Behaviour of Dioxins, Furans and Metals Associated with Stabilized Msw Combustor Ash in Sea Water', Chemistry and Ecology, 10: 3, 259 — 272
To link to this Article: DOI: 10.1080/02757549508037683
URL: http://dx.doi.org/10.1080/02757549508037683

Chemistry and Ecology, 1995, Vol. 10, pp. 259–272
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BEHAVIOUR OF DIOXINS, FURANS AND METALS ASSOCIATED WITH STABILIZED MSW COMBUSTOR ASH IN SEA WATER

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(Received 28 February 1994)

This report presents the results of a research programme designed to examine the engineering and environmental acceptability of stabilizing municipal solid waste (MSW) combustor ash for artificial reef construction. Municipal solid waste combustor ash was combined with Portland cement to form solid blocks using conventional construction block making technology. The resultant stabilized combustor ash (SCA) blocks were used to construct an artificial habitat in Conscience Bay, Long Island Sound, New York and compared to identical concrete blocks, fabricated using natural aggregates. Over a 4.5 year period divers periodically returned to the site to monitor the interaction of SCA blocks with the marine environment and compare the performance of these blocks with the concrete control blocks. Results show that the SCA blocks retain their strength after prolonged sea water exposure. Contaminants of environmental concern, including metals, dioxins and furans, were retained within the cementitious matrix of the SCA blocks after prolonged sea water submersion. In addition, organisms growing on the surfaces of the SCA blocks did not accumulate contaminants from the blocks.

KEY WORDS: Ash, artificial reefs, metal leaching, dioxin, furans

INTRODUCTION

In May 1985 a research programme was initiated at the Marine Sciences Research Center to examine the feasibility utilizing stabilized municipal solid waste (MSW) combustor ash for artificial reef construction in the ocean. Results of these studies showed that particulate combustion ash could be combined with cement to form a solid block possessing physical properties necessary for ocean disposal (Roethel *et al.*, 1987). The stabilized ash was subjected to regulatory extraction protocols and in no instance did the metal concentrations in the leachates exceed the regulatory limits for toxicity (Breslin *et al.*, 1988). Bioassays revealed no adverse impacts to the phytoplankton communities exposed to elutriate concentrations greater than could be encountered under normal disposal conditions (Roethel and Breslin, 1993). The success of the laboratory studies resulted in the issue of the necessary permits for the placement of an artificial habitat constructed using stabilized combustor ash in coastal waters.

During April 1987 and again during September 1988, stabilized combustor ash and concrete control blocks were submerged in eight metres of water in Conscience Bay, Long Island Sound, New York to form reef structures. The primary objectives of the investigation were to determine whether:

1) prolonged sea water exposure adversely affects the structural integrity of the SCA blocks;
2) metals of environmental concern leach from the SCA blocks;
3) organics such as polychlorinated dibenzodioxans (PCDD) and polychlorinated dibenzofurans (PCDF) are released into the marine environment from SCA blocks;
4) marine communities that colonize the artificial habitat incorporate within their tissues organics known to be enriched in MSW combustor ash; and,
5) artificial habitats constructed from the SCA blocks develop a diverse biological community of organisms in a manner similar to a control structure.

Since the placement of the artificial habitats, divers have returned periodically to the reef site to study the interactions of stabilized combustor ash with the marine environment. Stabilized ash blocks were retrieved from the reef site for physical and chemical testing. Compressive strengths of the ash blocks were measured to monitor their strengths following prolonged sea water exposure. Samples of ash blocks exposed to sea water were analyzed for metals, dioxins, and furans to determine if contaminants associated with particulate MSW combustor ash are effectively retained within the stabilized blocks. In addition, divers removed biomass from the surfaces of the blocks and bivalves that resided within the crevices of the structures for analysis of their tissues for possible uptake of dioxins and furans.

MATERIALS AND METHODS

Ash Block Placement and Sampling Activities

Municipal solid waste combustor ash for block making was collected on two separate occasions from two operational waste-to-energy facilities; the Westchester Resource Recovery Facility, Westchester County, New York in November 1986 and the Baltimore Resource Recovery Facility (RESCO), Baltimore, Maryland in August 1988. Ash blocks were manufactured on two occasions at the research facilities of the Besser Company at the Alpena Community College, Alpena, Michigan.

The 'Narrows' region of Conscience Bay, Long Island Sound was selected as the site for the reef placement (Figure 1). Stabilized ash blocks and concrete control blocks were submerged to a depth of eight metres at a site located within Conscience Bay. Thirty ash blocks and thirty concrete blocks were submerged on April 27, 1987 while forty ash blocks and forty concrete blocks were submerged on September 23, 1988 (Figure 2). Compressive strengths of the ash blocks at the time of placement in April 1987 and September 1988 were 1120 and 1020 psi, respectively.

Reef sampling activities occurred over a 4.5 year period from April 27, 1986 to September 11, 1991. Reef blocks were retrieved for the measurement of their engineering properties and analysis of dioxin, furan, and metal content. Biomass samples were also retrieved from the block's surface to evaluate the presence and concentration of dioxins and furans.

Inorganic analytical protocols can be found in Roethel *et al.*, 1993 and PCDD/PCDF protocols are presented in Wente, 1991, O'Keefe *et al.*, 1985 and Roethel *et al.*, 1990.

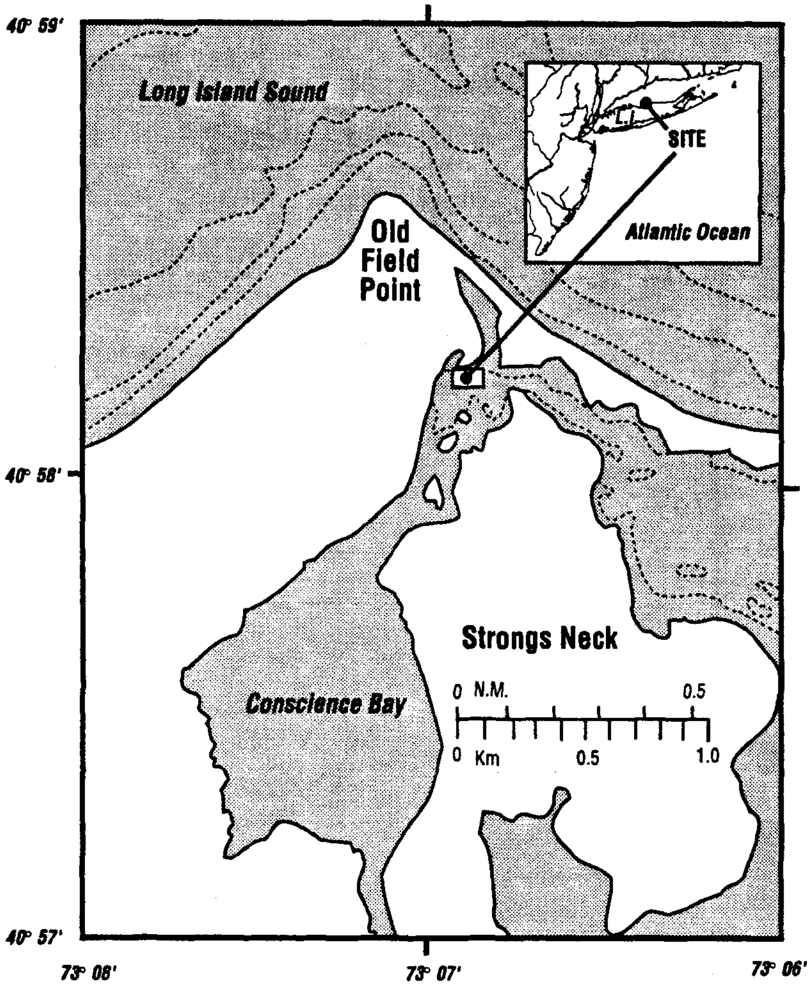

Figure 1 Ash and concrete block placement site, Conscience Bay, Long Island Sound, New York.

RESULTS AND DISCUSSION

Change in Ash Block Properties Following Sea Water Submersion

Major chemical elements in the ash blocks manufactured using Westchester combined ash during December, 1986 include calcium, magnesium, sodium, potassium, aluminium, silicon, iron, lead, zinc and copper (Table I). Chromium was present in minor amounts and cadmium was present as a trace component.

Major elements in the ash blocks manufactured using Baltimore RESCO combined ash during September, 1988 include calcium, magnesium, sodium, potassium, aluminium, silicon, iron, lead, zinc, and copper (Table I). Chromium was present in minor amounts and cadmium and arsenic as trace components.

Results of the engineering and metals analyses were normalized to pre-placement values allowing the use of both the April 1987 and September 1988 ash blocks to

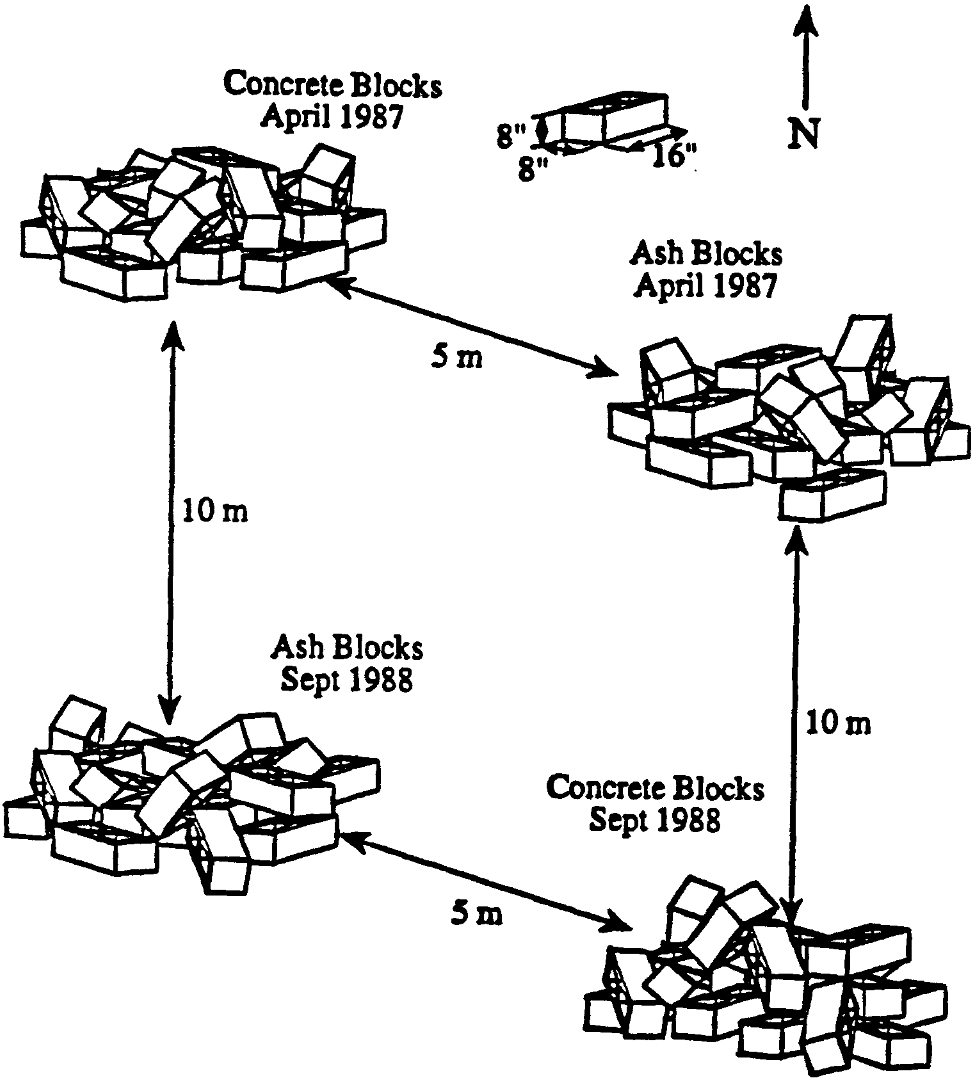

Figure 2 Ash and concrete block configuration following the April 1987 and September 1988 placement events.

determine the change in compressive strength and total metal content of ash blocks following placement. The percent retained of a physical or chemical property was calculated for each block following each sampling event. Percent retained was calculated as follows:

Percent Retained = $P_t/P_o \times 100$ where;

P_t = block physical or chemical property at time t.

P_o = initial block physical or chemical property.

Table I Elemental composition of SCA reef blocks; $HF\text{-}H_3BO_3$ acid digestion

Metal	April 1987 SCA Block	September 1988 SCA Block
Al (%)	4.17 (0.23)[a]	3.29 (0.11)
Si (%)	16.76 (0.22)	31.9 (0.47)
Fe (%)	7.25 (0.23)	7.45 (0.49)
Ca (%)	15.70 (1.6)	12.7 (1.0)
Mg (%)	1.13 (0.08)	1.24 (0.08)
Na (%)	2.39 (0.03)	4.51 (0.26)
K (%)	0.82 (0.05)	0.59 (0.02)
Zn (µg/g)	3760 (170)	2720 (134)
Pb (µg/g)	3580 (160)	2169 (502)
Cu (µg/g)	1260 (230)	1400 (300)
Cr (µg/g)	178 (15)	240 (22)
Cd (µg/g)	23.6 (1.5)	9.44 (2.1)
As (µg/g)	–[b]	20.9 (2.7)
Se (µg/g)	–[b]	<12

[a] Values in parentheses denote the standard deviation (n=3).
[b] – not determined.

The percent retained for each ash or concrete block property was plotted versus submergence time. A least squares linear regression analysis was performed on each data set. The significance of the regression analysis for each ash or concrete block property was calculated (Table II).

A student t-test was then used to determine if the slope of the regression line calculated for each property was significantly different from zero. A significant

Table II Regression Analysis of SCA Block Strength and Metal Content Following Submersion.

Parameter	r^2[a]	F-Statistic[b]	F Critical Value	Significance[c]
Block Strength				
Ash Block	0.116	1.70	4.60	N.S.
Concrete Block	0.843	64.87	4.67	S.
Block Metals				
Aluminium	0.007	0.09	4.67	N.S.
Arsenic	0.12	0.09	4.67	N.S.
Calcium	0.720	30.64	4.67	S.
Cadmium	0.240	3.43	4.75	N.S.
Chromium	0.117	1.59	4.67	N.S.
Copper	0.007	0.09	4.67	N.S.
Iron	0.183	2.68	4.67	N.S.
Potassium	0.306	5.30	4.67	S.
Magnesium	0.090	1.19	4.67	N.S.
Lead	0.006	0.07	4.67	N.S.
Silicon	0.051	0.34	4.67	N.S.
Sodium	0.067	0.93	4.67	N.S.
Zinc	0.654	22.72	4.67	S.

[a] Correlation coefficient obtained from regression analysis performed by the Least Squares method (Sokal and Rohlf, 1981).
[b] F-statistic: result of a one-way model I ANOVA test for the significance of the regression. Critical values were obtained from a table of critical values of the F-distribution.
[c] 95% significance level ($\alpha = 0.05$).

positive slope indicated an increase in the property of the block following submersion while a significant negative slope indicated a decrease in the property of the block following submersion (Table III).

Effects of Sea Water on Ash and Concrete Block Strength

Linear regression analysis of the compressive strength data yielded negative slopes for both the ash and concrete blocks. However, neither the regression line nor the slope of the line was significant for the ash block data (Table III). In contrast, both the correlation coefficient and the slope of the regression line were significant for the concrete block data.

Ash blocks retained 84% of their initial compressive strength following 4.5 years sea water submersion (Figure 3). Given the rate in the decrease in compressive strength, the compressive strength of the ash blocks would exceed the minimum compressive strength criteria for ash blocks in the sea of 300 psi for 20 years. In contrast, the compressive strength of concrete blocks retrieved from the reef site rapidly decreased following placement failing within three years following placement (Figure 3).

Metal Content of Ash Blocks Following Sea Water Submersion

Linear regression analysis of the metal data yielded positive slopes for iron, sodium, silicon and magnesium while negative slopes were calculated for aluminium, arsenic, calcium, cadmium, chromium, copper, potassium, lead and zinc (Table III). However, the regression line was only significant for calcium, potassium and zinc. Results of

Table III Determination of the Significance of the Slope of the Best-Fit Line for SCA Block Strength and Metal Content.

Metal	Slope[a]	t-Statistic[b] Value	t Critical	Significance[c]
Block Strength				
Ash Block	-0.0082	1.31	2.160	N.S.
Concrete Block	-0.0738	8.05	2.179	S.
Block Metals				
Aluminium	-0.0019	0.30	2.179	N.S.
Arsenic	-0.0082	2.52	2.571	N.S.
Calcium	-0.0251	5.54	2.179	S.
Cadmium	-0.120	1.85	2.201	N.S.
Chromium	-0.0067	1.26	2.179	N.S.
Copper	-0.0027	0.30	2.179	N.S.
Iron	0.0157	1.63	2.179	N.S.
Potassium	-0.0152	2.30	2.179	S.
Magnesium	0.0091	1.09	2.179	N.S.
Lead	-0.0019	0.26	2.179	N.S.
Silicon	0.0016	0.29	2.179	N.S.
Sodium	0.0054	1.33	2.179	N.S.
Zinc	-0.0179	4.77	2.179	S.

[a] Slope of the best-fit line obtained from regression analysis performed by the Least Squares method (Sokal and Rohlf, 1981).

[b] t-statistic: result of a t-test where the null hypothesis states that the slope of the line equals zero: h_0: $M_1 = 0$. Critical t-values were obtained from a table of critical values of the t-distribution.

[c] 95% significance level ($\alpha = 0.05$).

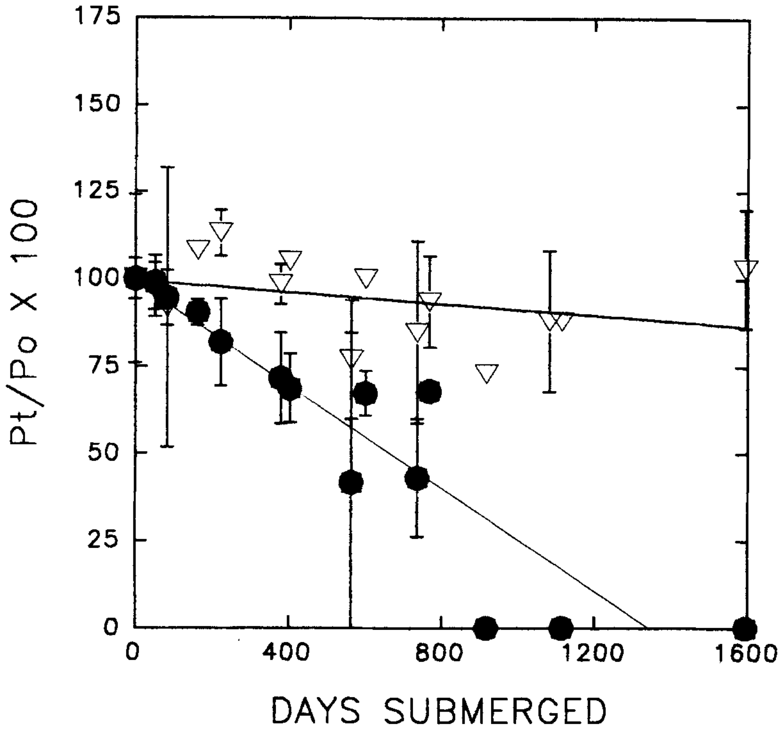

Figure 3 Compressive strength versus submergence time for concrete control (●) and SCA blocks (▽). Regression line (—) is also shown for each data set.

the Student's t-test showed that the slope of the best-fit line was also significantly different from zero for calcium, potassium and zinc (Table III).

Calcium, potassium and zinc yielded significant regression lines and had slopes significantly different from zero. Therefore, significant decreases in the calcium, potassium and zinc content of the ash blocks were observed as submergence time increased. For the remaining metals, aluminium, arsenic, chromium, cadmium, copper, iron, sodium, lead, and silicon, no significant trend in the data was observed.

Potassium loss is most likely due to soluble potassium compounds in the SCA blocks (Lobatka *et al.*, 1985). Zinc loss has been attributed to the dissolution of zinc metal in the SCA blocks due to electrochemical effects (Breslin and Roethel, 1994). Calcium loss from stabilized waste blocks in sea water has been reported in both laboratory and field studies (Roethel, 1981, Edwards and Duedall, 1985, Breslin, 1986, Woodhead *et al.*, 1984). The rate of calcium loss is affected, in part, by the block's pore water pH and sea water salinity. The block's calcium loss however, is compensated for by an ion exchange mechanism resulting in the block's uptake of magnesium from sea water.

Metals of environmental concern including lead, chromium, copper, and cadmium were effectively retained within the SCA blocks. The high alkalinity of the particulate MSW combustor ashes, the Portland type II cement additive, and the alkalinity of the sea water combine to create a favourable environment within the SCA blocks for the retention of metals.

PCDD/PCDF Concentrations in Combustor Ash and SCA Blocks

Comparative data on polychlorinated-p-dibenzodioxins (PCDD) and polychlorinated dibenzofurans (PCDF) are usually reported in terms of the total concentration of all dioxins and furans with four or more chlorine atoms per molecule and the concentration of 'toxic equivalents' (TE). Toxic equivalents are calculated by using weighting factors based on the relative toxicity of each of the many dioxins and furan isomers as compared to the most toxic, 2,3,7,8-TCDD. Table IV presents the calculated toxicity weighting factors for each homologue of PCDD/PCDF that, when multiplied by the concentration, yields the TE. The cumulative TE's provide the samples TE concentration. The TE concentrations associated with the combined ash were calculated according to EPA methods (USEPA, 1987; USEPA, 1990).

The PCDD/PCDF analyses of duplicate samples of the Baltimore combined combustor ash prior to stabilization are presented in Table V. All isomers were detected and found in concentrations typical of combined ash (Koppelman and Tanenbaum 1990; USEPA 1990). The 2,3,7,8-CDDs were detected in increasing concentration from lower to higher chlorination levels in each of the ash samples. TCDD concentrations ranged from 5.3 to 17 pg g^{-1} and OCDD from 1100 to 1400 pg g^{-1}.

Among the 2,3,7,8-CDFs, the hepta isomer was detected in the highest concentration with a range from 180 to 240 pg g^{-1}. The 2,3,7,8-TCDF identified in these analyses represents 2,3,7,8-TCDF and co-eluters. The Ultra 2 GC column used for the analysis is not isomer specific for 2,3,7,8-TCDF and several other isomers could co-elute at the same retention time. One sample showed no detectable 2,3,7,8-TCDF though we believe it is present. A shifting of the retention time just beyond

Table IV Toxicity Equivalency Factors Associated with PCDD/PCDF Homologue

Analyte	Toxicity Factor
2378TCDD	1
12378PCDD	0.5
123678HxCDD	0.04
123789HxCDD	0.04
123478HxCDD	0.04
1234678HpCDD	0.001
123467890CDD	0
2378TCDF	0.1
12378PCDF	0.1
23478PCDF	0.1
123478HxCDF	0.01
123678HxCDF	0.01
234678HxCDF	0.01
123789HxCDF	0.01
1234678HpCDF	0.001
123467890CDF	0
OTHER TCDD	0.01
OTHER PCDD	0.005
OTHER HxCDD	0.0004
OTHER HpCDD	0.00001
OTHER TCDF	0.001
OTHER PCDF	0.001
OTHER HxCDF	0.0001
OTHER HpCDF	0.00001

Table V PCDD/PCDF Concentrations and TE Values pg g^{-1} Measured in Combined Ash Samples

	Sample 1		Sample 2	
Analyte	Conc.	Toxicity Equivalency	Conc.	Toxicity Equivalency
2378TCDD	17	17	5.3	5.3
12378PCDD	19	9.5	17	8.5
123678HxCDD	48	1.92	31	1.24
123789HxCDD	65	2.6	42	1.68
123478HxCDD	26	1.04	17	0.68
1234678HpCDD	450	0.45	340	0.34
123467890CDD	1400	0	1100	0
2378TCDF	0	0	69	6.9
12378PCDF	44	4.4	32	3.2
23478PCDF	54	5.4	17	1.7
123478HxCDF	80	0.8	39	0.39
123678HxCDF	57	0.57	66	0.66
234678HxCDF	68	0.68	69	0.69
123789HxCDF	0	0	3.7	0.037
1234678HpCDF	240	0.24	180	0.18
123467890CDF	180	0	68	0
TOTAL TCDD	59	0.42	51	0.457
TOTAL PCDD	68	0.245	57	0.2
TOTAL HxCDD	290	0.0604	150	0.024
TOTAL HpCDD	740	0.0029	500	0.0016
TOTAL TCDF	540	0.54	310	0.241
TOTAL PCDF	350	0.306	170	0.138
TOTAL HxCDF	280	0.0075	210	0.00323
TOTAL HpCDF	310	0.0007	250	0.0007
TOTAL PCDD/PCDF	4217		2866	
TOTAL TE		46.18		32.56

the retention time tolerance would cause the peak present not to match with the standard.

The data in Table V indicate that PCDDs/PCDFs are present in extremely low but highly variable concentrations. Total concentrations measured for the duplicate samples ranged from 2870 to 4220 pg g^{-1}. The considerable variation between samples is attributed to the significant differences in the concentration of the higher chlorinated isomers.

Using weighted values reduces the variation between the samples providing a total 2,3,7,8-TCDD TE concentration that ranges between 32.5 to 46.2 pg g^{-1} (Table V). The total TE for each of these samples was substantially lower than the Center for Disease Control (CDC) recommended 2,37,7,8-TCDD Toxicity Equivalent limit of 1000 pg g^{-1} (1 part per billion) in residential soils (USEPA 1990; Kimbrough *et al.*, 1984).

Table VI presents the PCDD/PCDF concentrations and calculated TEs for each homologue measured in SCA blocks prior to, and following placement in the sea. A single sample analyzed prior to placement in the sea was found to contain 2,3,7,8-CDD concentrations ranging from 6.1 to 850 pg g^{-1} while the 2,3,7,8-CDF concentrations ranged from 2.4–140 pg g^{-1}. The concentrations of PCDDs/PCDFs associated with this sample were lower than that reported in Table V for the unstabilized ash. This is due, in part, to the addition of 15% Portland cement used as the stabilization additive. Reduction in concentrations beyond that explained by

Table VI PCDD/PCDF Concentrations and Toxicity Equivalent Values pg g^{-1} Measured in Submerged SCA Blocks

	Stabilized Ash Block Submersion Time (Days)									
	T=0 (n=1)		T=223 (n=3)		T=404 (n=2)		T=601 (n=2)		T=1082 (n=2)	
Analyte	Conc. (pg/g)	Tox. Equ. (pg/g)	Conc. (pg/g)	Tox. Equ. (pg/g)	Conc. (pg/g)	Tox. Equ. (pg/g)	Conc. (pg/g)	Tox. Equ. (pg/g)	Conc. (pg/g)	Tox. Equ. (pg/g)
2378TCDD	6.10	6.10	5.60 (0.9)	5.60 (0.9)	3.3 (0.0)	3.3 (0.0)	2.0 (0.5)	2.0 (0.5)	5.4 (1.4)	5.4 (1.4)
12378PCDD	14.00	7.00	14.67 (1.1)	7.33 (0.6)	7.95 (0.3)	3.98 (0.2)	8.4 (3.7)	4.2 (1.8)	18 (4.2)	9.0 (2.1)
123678HxCDD	26.00	1.04	26.33 (3.2)	1.05 (0.1)	13.0 (1.4)	0.52 (0.06)	15.0 (5.6)	0.6 (0.2)	31.5 (6.3)	1.26 (0.2)
123789HxCDD	34.00	1.36	43.33 (7.1)	1.73 (0.3)	15.0 (1.4)	0.60 (0.06)	19 (4.2)	0.8 (0.2)	44 (9.8)	1.76 (0.3)
123478HxCDD	17.00	0.68	14.97 (6.0)	0.60 (0.2)	9.15 (0.7)	0.37 (0.03)	10.2 (4.0)	0.4 (0.2)	21.5 (3.5)	0.86 (0.1)
1234678HpCDD	230.00	0.23	283.3 (51)	0.28 (0.05)	109 (15)	0.11 (0.01)	200 (84)	0.2 (0.08)	340 (70)	0.34 (0.07)
123467890CDD	850.00	0.00	1016 (246)	0.00	355 (63)	0.00	670 (211)	0.00	1200 (280)	0.00
2378TCDF	6.60	0.66	35.0 (31)	3.5 (3.1)	0.00	0.00	72.5 (34)	7.23 (3.4)	101 (27)	10.1 (2.7)
12378PCDF	30.00	3.00	29.7 (4.6)	2.97 (0.5)	14.0 (1.4)	1.4 (0.1)	123 (108)	12.4 (11)	75 (33)	7.5 (3.3)
23478PCDF	31.00	3.10	24.3 (25)	2.43 (2.5)	23.5 (3.5)	2.35 (0.3)	60.5 (47)	6.1 (4.7)	63 (17)	6.3 (1.7)
123478HxCDF	48.00	0.48	49.0 (19)	0.49 (0.2)	29.0 (2.8)	0.29 (0.03)	196 (176)	1.9 (1.7)	92 (26)	0.92 (0.2)
123678HxCDF	34.00	0.34	58.3 (20)	0.58 (0.2)	16.0 (1.4)	0.16 (0.01)	61 (45)	0.61 (0.4)	47 (9.8)	0.47 (0.09)
234678HxCDF	33.00	0.33	64.0 (41)	0.64 (0.4)	13.0 (4.2)	0.13 (0.04)	24.5 (10)	0.25 (0.1)	49 (9.8)	0.49 (0.09)
123789HxCDF	2.40	0.02	4.47 (5.1)	0.04 (0.05)	0.50 (0.7)	0.01 (0.01)	8.3 (8.1)	0.8 (0.8)	3.1 (0.2)	0.03 (0.002)
1234678HpCDF	140.00	0.14	157 (20)	0.16 (0.02)	61.5 (7.8)	0.06 (0.01)	105 (36)	0.1 (0.03)	170 (28)	0.17 (0.02)
123467890CDF	57.00	0.00	63.0 (11)	0.00	22.0 (4.2)	0.00	35.0 (9.8)	0.00	67 (11)	0.00
TOTAL TCDD	59.00	0.53	52.3 (38)	0.47 (0.3)	41.5 (13)	0.38 (0.1)	24.5 (10)	0.22 (0.1)	81 (41)	0.75 (0.4)
TOTAL PCDD	90.00	0.38	73.3 (58)	0.29 (0.29)	58.0 (14)	0.25 (0.07)	41.5 (23)	0.16 (0.09)	165 (35)	0.74 (0.1)
TOTAL HxCDD	190.00	0.05	163 (77)	0.03 (0.03)	99.5 (15)	0.02 (0.0)	111 (40)	0.02 (0.01)	345 (63)	0.10 (0.01)
TOTAL HpCDD	430.00	0.002	447 (152)	0.001637	210 (28)	0.001 (0.0)	345 (134)	0.001 (0.0004)	665 (148)	0.003 (0.0007)
TOTAL TCDF	360.00	0.35	353 (257)	0.32 (0.3)	330 (0.0)	0.33 (0.0)	300 (127)	0.23 (0.09)	595 (106)	0.49 (0.07)
TOTAL PCDF	290.00	0.23	239 (211)	0.19 (0.18)	210 (28)	0.19 (0.04)	420 (311)	0.28 (0.2)	595 (162)	0.46 (0.1)
TOTAL HxCDF	200.00	0.01	237 (58)	0.01 (0.01)	125 (21)	0.01 (0.0)	400 (311)	0.01 (0.007)	435 (92)	0.02 (0.004)
TOTAL HpCDF	180.00	0.0004	220 (10)	0.0002 (0.0)	82.5 (10)	0.0004 (0.0)	160 (70)	0.0006 (0.0003)	230 (420)	0.0006 (0.0001)
TOTAL PCDD/PCDF	2706.00		2860 (1080)		1510 (198)		2510 (1250)		4380 (986)	
TOTAL TE		26.03		28.7 (3.2)		14.4 (1.1)		37.8 (25)		47.1 (13.5)

Numbers in parentheses are standard deviations.
'n' is the number of samples analyzed.
T is the time in days.

dilution is observed for certain isomers and may be the result of an encapsulation of the ash particles by the Portland cement, thereby reducing the extraction efficiency.

The total PCDD/PCDF concentration measured for the pre-placement SCA block was 2706 pg g^{-1}. The total 2,3,7,8-TCDD TE concentration was 26.0 pg g^{-1}, a reduction of approximately 30% when compared to the mean TE calculated for the unstabilized combined combustor ash.

Blocks retrieved on May 4, 1989, after 223 days of submersion, were analyzed in triplicate for their PCDD/PCDF concentrations (Table VI). The 2,3,7,8-TCDD concentrations were similar for all three samples, ranging between 4.7 to 6.6 pg g^{-1}, mean 5.6 pg g^{-1}. As the chlorination levels increased, the variation between the samples also increased. The three 1,2,3,4,6,7,8,9-OCDD samples ranged in concentration between 850–1300 pg g^{-1}. The variability observed in the higher chlorinated homologues affected the total PCDD/PCDF concentrations for all three samples. These concentration ranged between 2165–4110 pg g^{-1} resulting in a mean concentration of 3010 ± 74 pg g^{-1}.

In so far as the higher chlorinated homologues contribute little to the 2,3,7,8-TCDD TE concentration, the calculated concentrations presented have a much smaller variation. The total 2,3,7,8-TCDD TE values for the three samples ranged between 26.0–32.2 pg g^{-1} providing a mean value of 28.7 ± 3.2 pg g^{-1}. The total TE values observed for the stabilized ash blocks that were submerged in the sea for approximately seven months bracketed the TE values obtained in the pre-placement blocks.

Both SCA and concrete control blocks were retrieved for PCDD/PCDF analysis on November 1, 1989 after 404 days of submersion. Results of analysis of duplicate samples of the reference concrete block revealed that with the exception of OCDD, no PCDDs or PCDFs were detected. The presence of the OCDD, 38 and 39 pg g^{-1} for the two samples, is not unusual since it is a persistent contaminant in the laboratory as well as in the field (Roethel *et al.*, 1990).

Similar PCDD/PCDF concentrations were detected for the two SCA blocks retrieved following 404 days of submersion (Table VI). The slightly higher concentrations observed in one of the samples may be due to the higher sensitivity and lower detection limits associated with that analysis. The sum of the total tetra through hepta dioxins and tetra through hepta furans were 459 and 790 pg g^{-1} for one sample and 359 and 705 pg g^{-1} for the second sample. Total dioxins were detected in increasing concentrations from lower to higher chlorination levels whereas the total furan isomers were detected in decreasing concentration from lower to higher chlorination levels. Total PCDD/PCDF concentrations for the two samples were 1370 to 1650 pg g^{-1} mean 1510 ± 198 pg g^{-1}.

The total 2,3,7,8-TCDD TE concentrations for these two samples were 13.6 and 15.3 pg g^{-1}; when compared with the two previous samples; this is a substantially lower total PCDD/PCDF concentration and total TE concentration. Approximately 50% of the total TE concentration associated with the sample removed in May 1989 was found in this sample. While some of the differences between the samples can be attributed to lower GC/MS sensitivity, higher detection limits and, in one case, a possible shift in retention time resulting in two isomers exhibiting no detectable concentration, it is still difficult to explain the reduction in measured concentrations.

On May 18, 1990, after 601 days of submersion, SCA blocks were retrieved from the study site for PCDD/PCDF analysis. Considerable differences in concentrations, especially at the higher chlorination levels, between the two samples were observed (Table VI). Total PCDD/PCDF concentrations ranged between 1620 to 3309 pg g^{-1}, mean 2510 ±1250 pg g^{-1}. Unlike previous analyses, the total 2,3,7,8-TCDD TE concentrations exhibited substantial variation ranging from 20.1–55.5 pg g^{-1}. The largest contribution to the variation observed between samples is attributed to the significantly higher CDF concentrations associated with one of the two samples. CDF concentrations appear to be enriched approximately five-fold in one sample when compared with the second while CDD concentrations appear similar between the two samples.

The final sample removed for PCDD/PCDF analysis was retrieved on September 11, 1991, after 1082 days of submersion. The results show that duplicate analyses shows PCDD/PCDF concentrations with variation similar to previous analyses. As observed above, the higher chlorinated CDDs and the CDFs are responsible for the lack of similarity between samples. Total PCDD/PCDF concentrations were 3680 and 5075 pg g^{-1}, mean 4380 ± 986 pg g^{-1}. The total 2,3,7,8-TCDD TE values for the two samples were 37.6 and 56.7 pg g^{-1}, mean 47.1 ± 13.5 pg g^{-1}. These values are higher than any previously observed and result in a total 2,3,7,8-TCDD TE value that is approximately 50% higher than the pre-placement value.

A comparison of all the PCDD/PCDF data associated with the effects of sea water submersion on dioxin and furan mobility reveals that the total 2,3,7,8-TCDD TE values ranged from a low of 14.4 pg g^{-1} to a high of 47.1 pg g^{-1}. This compares to a pre-placement 2,3,7,8-TCDD TE concentration of 26.0 pg g^{-1}. While there is variation in the PCDD/PCDF data with time that can be attributed to the non-homogeneity of these organic compounds in the ash and thereby the stabilized blocks, it would appear that over the three years of submersion, the stabilized ash blocks were not releasing PCDD/PCDF constituents into the marine environment.

PCDD/PCDF Content of Attached Biomass

The PCDD/PCDF concentrations measured in the hydroid biomass collected from both the SCA and concrete control blocks on June 8, 1989, after 258 days of submersion. In two of the three SCA samples collected, concentrations of all PCDD/PCDF analytes were found in concentrations below the detection limits of the analytical protocol. For one sample, 1,2,3,4,6,7,8,9-OCDD was found at a concentration of 1400 pg g^{-1}. No other PCDD/PCDF in these samples were above the analytical detection limits.

All three samples of hydroid biomass removed at this time from the concrete blocks revealed the presence of 1,2,3,4,6,7,8,9-OCDD ranging between 870–1400 pg g^{-1}. One sample was found to contain 15 pg g^{-1} 2,3,7,8-TCDF and 55 pg g^{-1} 1,2,3,4,6,7,8-HpCDD. For another sample, in addition to OCDD, 110 pg g^{-1} OCDF was detected. It is not unreasonable for OCDD and OCDF to be detected when no other isomers are observed since it is the most widely dispersed of all the PCDDs and PCDFs in the environment.

Mussel Biomass

Results show that no 2,3,7,8-substituted tetra through hepta dioxins were detected in mussel tissues collected on July 10, 1989 (290 days of submersion) from the SCA blocks. OCDD concentrations ranged from 27 to 54 pg g^{-1}, which was within the range detected in the method blanks. The presence of 2,3,7,8-TCDF (and/or co-eluters) was the only 2,3,7,8-substituted dibenzofuran detected in these samples. Concentrations ranged from below detection limit to 14 pg g^{-1}. Mussel samples removed on July 10 from the concrete reef and analyzed in triplicate had similar concentrations of both OCDD and TCDF.

No 2,3,7,8-substituted tetra through hepta dioxins were detected in mussels removed from the stabilized ash reef on August 17, 1989 after 328 days of submersion. OCDD concentrations ranged from 29 to 51 pg g^{-1}. 2,3,7,8-TCDF was found in two of the three samples analyzed in concentrations of 8.9 and 13 pg g^{-1}.

Mussels removed from the concrete reef and analyzed for PCDD/PCDF on this date were found to contain similar concentrations of both OCDD and 2,3,7,8-TCDF when compared to the mussel tissue associated with the SCA blocks. OCDD concentrations ranged from 50–130 pg g^{-1}, while 2,3,7,8-TCDF was found within the range below detection limits to 14 pg g^{-1}. No other PCDD or PCDF compounds were detected in these samples.

CONCLUSIONS

Particulate MSW combustor ash, when combined with Portland cement, can be stabilized successfully into solid blocks using conventional block making technology. On April 27–28, 1987 and again on September 23, 1988 ash blocks and concrete control blocks were successfully transported and placed in Conscience Bay, Long Island Sound, New York to form artificial reef structures.

The establishment of the Conscience Bay reef site constructed using stabilized ash blocks has provided an opportunity to study the *in situ* interactions of these blocks with the marine environment. Results of this study have shown that the stabilized ash blocks have retained their strengths after prolonged sea water exposure. Metals of environmental concern, including lead and cadmium, are retained within the cementitious matrix of the ash blocks following 4.5 years of submersion at the reef site.

The behaviour of dioxins and furans associated with the MSW combustor ash, following submersion in the sea, suggest that these organic compounds do not leach from stabilized combustion ash blocks. The biological community associated with the ash blocks, when analyzed for the presence of dioxins and furans, were found to have concentrations of these compounds similar to those found in identical organisms removed from the concrete control blocks. The data suggests that PCDDs and PCDFs are tightly bound to the ash particle and not released into the marine environment. In addition, PCDDS and PCDFs are not actively assimilated by the attached biological reef community.

To date, no adverse environmental impacts have been observed at the Conscience Bay reef site due to the presence of ash blocks.

Acknowledgements

We thank the New York State Department of Health and especially Dr. Kenneth Aldous for conducting the PCDD/PCDF analyses. In addition, we thank Chris Stein, Maryann Meartz-Wente, Victor Schaeperkoetter, Andrew Parrella, Byeong-Gweon Lee and John Gordy for their assistance in the sampling and analysis. We thank State Senator Cesar Trunzo and Mr. George Proios, for their support in obtaining funds for this research project from the New York State Legislature.

This work was supported by grants from the US Environmental Protection Agency and the New York State Legislature.

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