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Project Summary

Mobility of Dioxins, Furans and Trace Metals from Stabilized MSW Combustor Ash in Seawater

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This report presents the results of a research program designed to examine the engineering and environmental acceptability of stabilizing municipal solid waste (MSW) combustor ash for artificial reef construction. MSW combustor ash was combined with Portland cement to form solid blocks using conventional block making technology. The resultant stabilized combustor ash (SCA) blocks were used to construct an artificial habitat in Conscience Bay, Long Island Sound, N.Y.

Divers periodically returned to the site to monitor the interaction of SCA blocks with the marine environment over a 4.5-yr period. Results show that the SCA blocks retain their strength after prolonged seawater exposure. Contaminants of environmental concern, including metals, dioxins and furans, were retained within the cementitious matrix of the SCA blocks after prolonged seawater submersion. In addition, organisms growing on the surfaces of the SCA blocks are not accumulating contaminants from the blocks.

This Project Summary was developed by EPA's Risk Reduction Engineering Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back)

Introduction

In May 1985 a research program was initiated at the Marine Sciences Research Center to examine the feasibility of utilizing stabilized 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. 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. Bioassays revealed no adverse impacts to the phytoplankton communities exposed to elutriate concentrations higher than could be encountered under normal disposal conditions. The success of the laboratory studies resulted in securing the necessary permits for the placement of an artificial habitat constructed of 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 meters of water in Conscience Bay, Long Island Sound, N.Y., to form reef structures. The primary objectives of the investigation were to determine:

1) whether prolonged seawater exposure adversely impacts the structural integrity of the stabilized combustor ash (SCA) blocks,
2) whether metals of environmental concern leach from the SCA blocks,
3) whether organics such as PCDDs and PCDFs are released into the marine environment from SCA blocks,
4) whether marine communities that colonize the artificial habitat incorporate within their tissues metals

and/or organics known to be enriched in MSW combustor ash, and,

5) whether 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 periodically returned 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 the strengths of the blocks following prolonged seawater exposure. Samples of ash blocks. exposed to seawater 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 metals, dioxins and furans.

Materials and Methods

Ash Block Placement and Sampling Activities

MSW 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, NY, in November 1986 and the Baltimore RESCO facility, Baltimore, MD in August 1988. Ash block manufacturing was conducted on two occasions at the research facilities of the Besser Company at the Alpena Community College, Alpena, MI.

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 meters at the 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 blocks at the time of placement were 1120 and 1020 psi for April 1987 and September 1988 ash blocks, respectively.

Reef sampling activities occurred over a 4.5-yr period from April 27, 1986, to September 11, 1991. Reef blocks were retrieved for the determination of their engineering properties and dioxin, furan, and

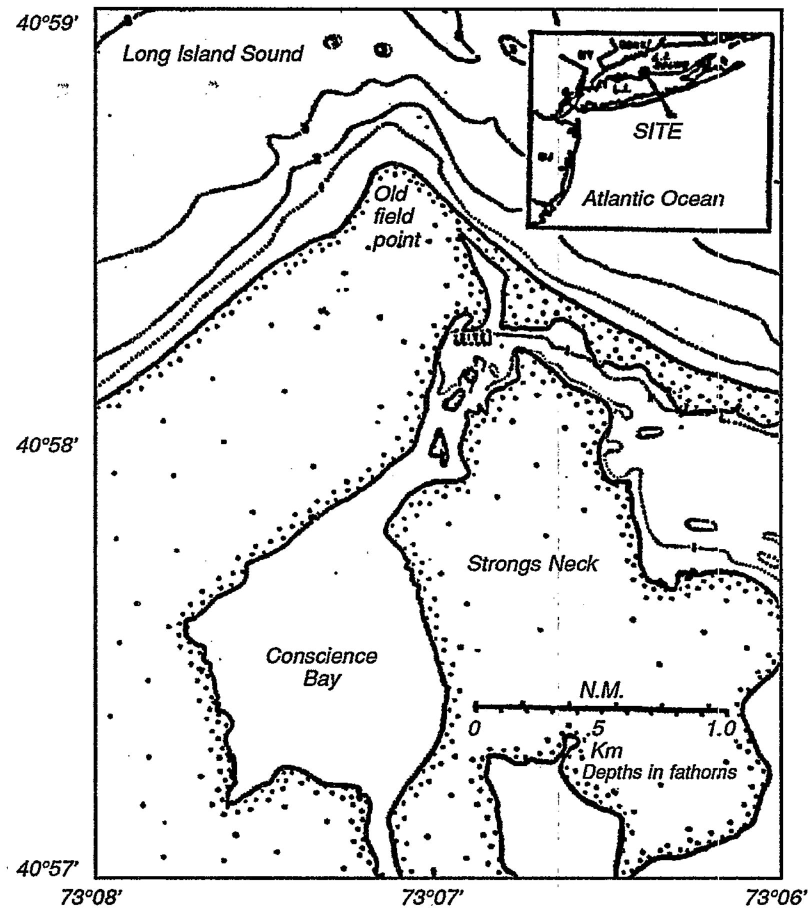

Figure 1. Ash and concrete block placement site, Conscience Bay, Long Island Sound, NY

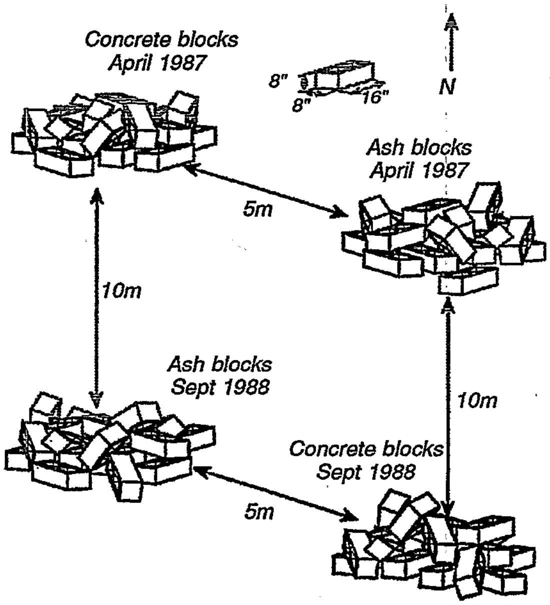

Figure 2. Ash and concrete block configuration following the April 1987 and September 1988 placement events.

metal content. Biomass samples were also retrieved for the analysis of tissue dioxin, furan, and metal content.

Results and Discussion

Change in Ash Block Properties Following Seawater Submersion

Results of the engineering and metals analyses were normalized to allow the use of both the April 1987 and September 1988 ash blocks to 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 = $P_t/P_0 \times 100$ where;
P_t = block physical or chemical property at time t.
P_0 = initial block physical or chemical property (Table 1).

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 to obtain a best-fit line. The significance of the regression analysis for each ash or concrete block property was then determined (Table 2).

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 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 3).

Table 1. Elemental Composition of Stabilized Ash Reef Blocks: HF-H_3BO_3 Acid Digestion

Metal	April 1987 Ash block	September 1988 Ash block
Al (%)	4.17 (0.23)[a]	3.29 (0.11)
Si (%)	16.76 (0.22)	21.9 (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)
Mn (µg/g)	1020 (70)	1040 (60)
Ba (µg/g)	ND[b]	1120 (98)
Cr (µg/g)	178 (15)	240 (22)
Cd (µg/g)	23.6 (1.5)	9.44 (2.1)
As (µg/g)	ND	20.9 (2.7)
Se (µg/g)	ND	<12
Hg (µg/g)	ND	<1.0
Ag (µg/g)	ND	<6.0

[a] Values in parenthesis denote the standard deviation (n=3).
[b] ND = this element was not determined.

Effects of Seawater 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 3). 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-yr seawater submersion (Figure 3). Given the rate in the decrease in compressive strength, the compressive strength of the ash blocks would exceed the minimum compressire strength criteria for ash blocks in the sea of 300 psi for 20 yr. In contrast, the compressive strength of concrete blocks retrieved from the reef site continuously decreased following placement.

Table 2. Regression Analysis of Physical and Chemical Ash Block Properties

	r^2	F Statistic[1]	F Critical Value	Significance[2]
Block Strength				
Ash Block	0.1160	1.700	4.60	N.S.
Concrete Block	0.8430	64.87	4.67	S.
Block Metals				
Aluminum	0.0176	0.2247	4.67	N.S.
Arsenic	0.1816	0.9222	5.99	N.S.
Barium	0.3572	1.579	5.99	N.S.
Calcium	0.7092	31.712	4.67	S.
Cadmium	0.1633	2.343	4.67	N.S.
Chromium	0.3232	3.175	4.67	N.S.
Copper	0.0029	0.0039	4.67	N.S.
Iron	0.1479	2.256	4.67	N.S.
Potassium	0.1243	1.844	4.67	N.S.
Magnesium	0.4981	4.322	4.67	N.S.
Manganese	0.0031	0.0406	4.67	N.S.
Sodium	0.0667	0.9303	4.67	N.S.
Lead	0.0029	0.0388	4.67	N.S.
Silicon	0.0026	0.0341	4.67	N.S.
Zinc	0.4872	12.351	4.67	S.

[1] F-Statistic: result of one way, Model I ANOVA testing for the significance of regression. Critical values were obtained from a table of critical values of the F-distribution for α=.05.
[2] Regression performed by Least Squares method.

Table 3. Determination of the Significance of the Slope of the Best-fit Line for Physical and Chemical Ash Block Properties

	Slope	t Statistic[1]	t Critical value	Significance[2]
Block Strength				
Ash Block	-0.0082	1.310	2.160	N.S.
Concrete Block	-0.0738	8.050	2.160	S
Block Metals				
Aluminum	0.0010	0.2841	2.179	N.S.
Arsenic	-0.0183	2.5271	2.571	N.S.
Barium	-0.0277	3.265	2.571	S.
Calcium	-0.0283	10.992	2.179	S.
Cadmium	-0.0067	1.708	2.179	N.S.
Chromium	0.0038	1.047	2.179	N.S.
Copper	-0.0006	0.109	2.179	N.S.
Iron	0.0101	1.858	2.179	N.S.
Potassium	-0.0249	5.96	2.179	S.
Magnesium	0.0276	4.657	2.179	S.
Manganese	-0.0014	0.373	2.179	N.S.
Sodium	0.0054	1.327	2.179	N.S.
Lead	-0.0029	0.706	2.179	N.S.
Silicon	0.0015	0.2929	2.179	N.S.
Zinc	-0.0108	4.123	2.179	S.

1 t-Statistic: result of t-test where 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.

2 95% significance level ($\alpha=.05$).

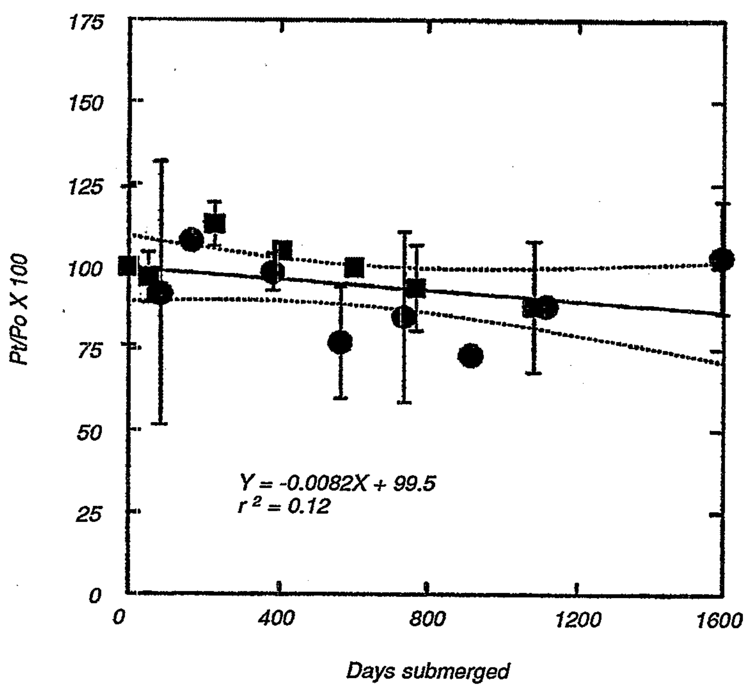

Figure 3. Compressive strength versus submergence time for April 1987 (●) and September 1988 (■) ash blocks. Regression line (——) and 95% confidence intervals (---) are also shown for the pooled data.

Metal Content of Ash Blocks Following Seawater Submersion

Linear regression analysis of the metal data yielded positive slopes for aluminum, chromium, iron, sodium, silicon and magnesium while negative slopes were calculated for arsenic, barium, calcium, cadmium, copper, potassium, manganese, lead and zinc (Table 3). However, the regression line was only significant for calcium and zinc. Results of the students t-test showed that the slope of the best-fit line was also significantly different from zero for calcium, and zinc (Table 3).

Calcium and zinc yielded significant regression lines and possessed slopes which were significantly different than zero. Therefore, significant decreases in the calcium and zinc content of the ash blocks was observed as submergence time increased (Figure 4). For the remaining metals-aluminum, arsenic, barium, chromium, cadmium, copper, iron, potassium, manganese, sodium, lead, and silicon no-significant trend in the data was observed (Figure 5).

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

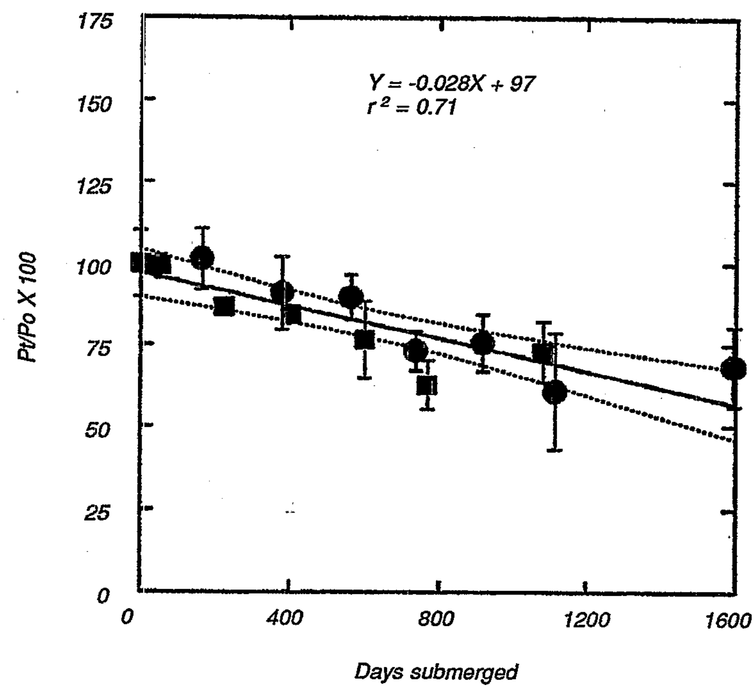

Figure 4. *Calcium content versus submersion time for April1987 (●) and September 1988 (■) ash blocks. Regression line (——) and 95% confidence intervals (---) are also shown for the pooled data.*

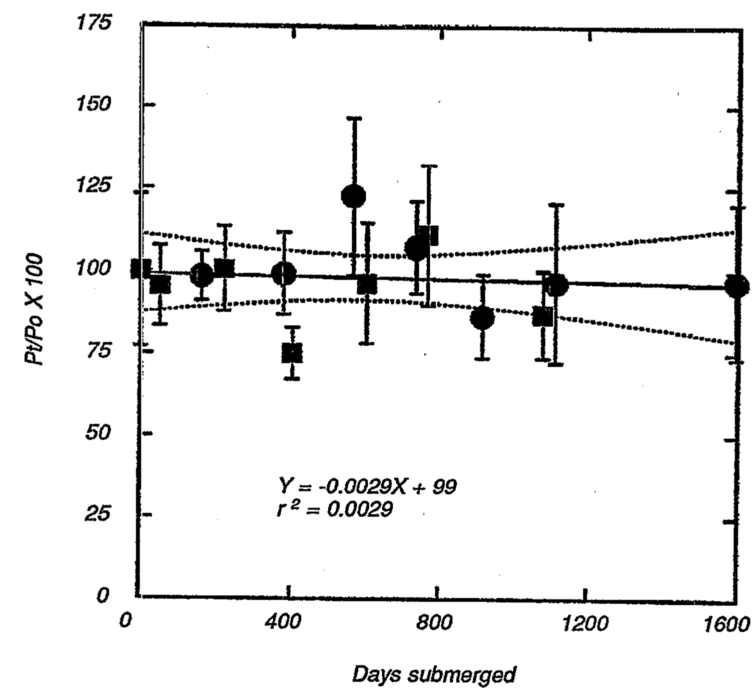

Figure 5. *Lead content versus submersion time for April1987 (●) and September 1988 (■) ash blocks. Regression line (——) and 95% confidence intervals (---) are also shown for the pooled data.*

Effects of Seawater Exposure on PCDD/PCDF Mobility

Following ash block submersion, the measured 2,3,7,8 tetra and octa dioxin and furan mean concentrations did not show any significant trend as a function of seawater exposure (Figure 6). Concentrations of PCDDs and PCDFs in the submerged ash blocks ranged over three orders of magnitude. During the 3 yr of seawater submersion, the mean 2,3,7,8-TCDD concentrations ranged between 2-6 pg/g. The 2,3,7,8 OCDF and 2,3,7,8-TCDF concentrations were approximately one order of magnitude higher, with mean concentrations. ranging between 60-100 pg/g. An analytical error is responsible for the TCDF value depicted in Figure 6 on the 404 day following submersion. The highest PCDD/PCDF concentrations were associated with the presence .of OCDD in the ash blocks. Measured 2,3,7,8-0CDD concentrations ranged from 850-1000

A slight reduction was observed for all PCDD/PCDF constituents on the 404 day and 601 day sampling events (Figure 6). These observed reductions are most likely associated with the non-homogeneity of MSW combustor ash used in the fabrication of the stabilized ash blocks as opposed to leaching of PCDD/PCDFs from the stabilized.ash blocks.

Conclusions

Particulate MSW combustor ash, when combined with portland cement, can be successfully stabilized 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, NY to form artificial reef structures.

The establishment of the Conscience Bay reef site constructed of stabilized ash blocks has provided a unique 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 seawater exposure. Metals of environmental concern, including lead and cadmium, are retained within the cementitious matrix of the ash blocks following 4.5 yr of submersion at the reef site. Organisms growing on the surfaces of the ash blocks, in addition to bivalves removed from the crevices of the artificial habitats, did not accumulate metals from the blocks.

The behavior of dioxins and furans associated with the MSW combustor ash,

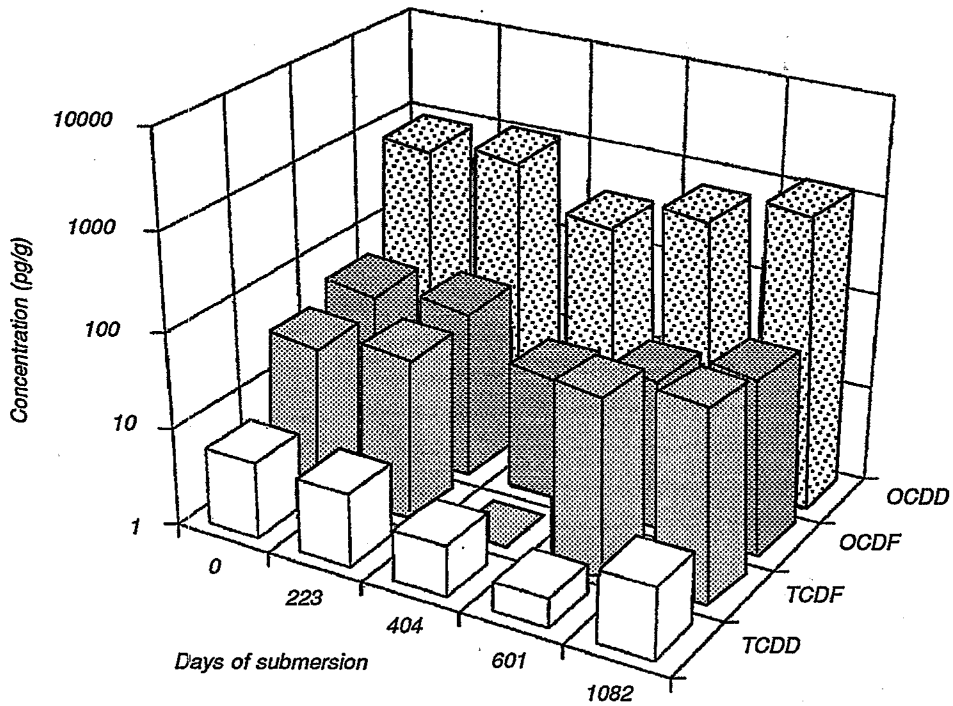

Figure 6. *Mean PCDD/PCDF concentrations measured in submerged ash blocks.*

following submersion in the sea, suggest that these organic compounds do not leach from the SCA 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 suggest that PCDDs and PCDFs affiliated with the stabilized ash blocks 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.

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