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The use of coal fly ash in concrete for marine artificial reefs in the southeastern Mediterranean: compressive strength, sessile biota, and chemical composition

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To examine the possible use of coal fly ash (CFA) in concrete for artificial reefs, blocks containing 0%, 40%, 60%, and 80% CFA as a substitute for sand were deployed in the Mediterranean at 18.5-m depth off the coast of Israel during a period of 33 months. Changes in compressive strength, composition, and coverage of sessile biota species, as well as in trace element concentration of the block surface and in sessile biota from four taxonomic groups, were determined as a function of time at sea and block type. Compressive strength clearly increased with time in all types to values well above the minimal strength considered necessary for stability of the blocks at sea. Moreover, the 40% and 60% CFA blocks were 1.5 times stronger than the 0% and 80% ones. Main sessile taxa recorded were filamentous green algae, bryozoa, barnacles, serpulid polychaeta, hydrozoa, and bivalves. Number of species settled and biotic coverage varied among block side and seasonally, but did not differ significantly between block types. The initial heavy metal composition (Hg, Cd, Pb, Cu, Zn, Cr, Mn, Fe, Al) of the block material was directly proportional to the CFA percentage. At the end of the study, Pb had decreased in all types, Cd in the 60% CFA block, and Fe and Al in the 40% and 60% blocks, while Mn had increased in the blocks with 0% and 80% CFA. After 21 months at sea, the only detectable change was a decrease in Pb concentration in all types, indicating that changes may be due to long-term processes. Trace metal levels (Hg, Cd, Zn, Mn, Cu, Fe, and Al) were measured in the sessile biota (hydrozoa, polychaeta, and bivalvia). In most cases, no dependence was found between metal levels and time at sea or CFA content of the blocks. In the hydroid, metal concentration even decreased over time.

Keywords: artificial reef, biotic coverage, coal fly ash, compressive strength, sessile biota, southeastern Mediterranean, species composition, stabilization, trace metal.

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Introduction

The growing interest in artificial reefs has expanded the quest for building materials that are stable and inert at sea. One suggested solution is to utilize waste products in an environmentally safe manner so as to increase material recycling and to decrease the need for waste disposal. Among the waste products that might be utilized are the combustion products of coal-fired electric power plants. Israel produced 8.6 million tonnes of Coal Fly Ash (CFA) between 1982 and 1998. About 72% was used by the cement industry as an additive, 14% was disposed of in the deep sea, and the remainder was used for other terrestrial applications (Kress *et al.*, 1993; Kress, 1993). Presently, the average yearly production is ca. 800 000 tonnes year^{-1}. Bulk disposal of excess CFA on land or at sea poses environmental problems, mainly because of leaching of elements, in particular heavy metals. In a consolidated form, CFA is more stable (Labotka *et al.*, 1985; Roethel and Oakley, 1985; van der Sloot *et al.*, 1985; Hockley and van der Sloot, 1991; Collins *et al.*, 1994; Sampaolo and Relini,

Table 1. Proportions of standard quartz sand to CFA (SQS:CFA; % weight) and water/cement fraction (W/C) in concrete containing 15% commercial C.P. 300 Portland cement ("Nesher" Industries, Israel) as used in the four treatments.

Treatment	SQS:CFA	W/C
Control (0% CFA)	85:0	1.00
40% CFA	45:40	1.05
60% CFA	25:60	1.13
80% CFA	5:80	1.30

1994; Collins and Jensen, 1995; Kuo *et al.*, 1995) and thus has been considered for the building of artificial reefs, artificial islands, and other underwater, man-made structures. If this application could be proven to have no detrimental effects on the marine environment, it may have positive economic and environmental implications through the recycling of waste material and preservation of alternative natural resources, such as quarry rocks and sand.

Within the framework of a feasibility study into using Israeli CFA as a substitute for sand in the construction of artificial reefs, our objectives were to examine relevant physical, chemical, and biological aspects of four block types deployed for different times at sea and subjected to local natural hydrographic conditions. We determined the compressive strength of the blocks (a proxy for block integrity) and evaluated the effects of block type on the settlement of marine biota, on metal leaching from the blocks and on bio-accumulation in the sessile biota, all as a function of time at sea.

Materials and methods

Four treatment groups of twenty 20 × 20 × 40 cm blocks were prepared in the National Building Research Institute (NBRI). Two tonnes of clean (no oil) CFA from the Orot Rabin power plant, Hadera, originating from burning a typical coal mixture (50% from the Greenside mine in South Africa and 50% from the Baily mine, USA), were used for this purpose. The four groups included a control block type (no CFA) and three block types containing 40%, 60%, and 80% CFA, respectively (see also Table 1). The concrete mixtures included 15% commercial C.P. 300 Portland cement ("Nesher" Industries, Israel, no CFA additives). Two narrow plastic pipes were set in the centre of each block for future attachment to the carrying tables using plastic wire ties. Each block was labelled during the casting. The blocks were than kept in freshwater containers for 27 days before being arranged randomly on 16 inert Plexiglas tables, 5 blocks per table (Figure 1). The tables with the blocks were deployed on November 1996 at 18.5 m water depth off the coast of Haifa (32°50′N, 34°56′E), 70 m northwest of "used-tyre" artificial reefs deployed in 1983 (Spanier *et al.*, 1990; Spanier, 2000). The tables were arranged in a Latin square design (Zar, 1984), enabling similar exposure of the blocks to environmental conditions and random sampling. SCUBA divers retrieved two blocks from each treatment group every 3 months in the first 2 years of the study, and every 4 months in the last year. A total of 10 samplings were performed after 3, 6, 9, 12, 15, 18, 21, 25, 29, and 33 months at sea.

Sampled blocks were transferred within 1 h to the laboratory. Biota were identified to the lowest taxonomic level possible (usually species) and their numbers on each of four sides (bottom, left, right, top) were determined by visual inspection under a stereoscope. Photographs of 10 × 14 cm rectangles were taken from each side of every block and converted, by scanning, to computer images. The relative coverage of each taxon identified in each image was calculated by image analysis software (TINA 2.07, Raytest). Multiple two-tailed paired t-test was used to compare number of settled species on each side among the CFA treatments for all sampling events combined. One-way ANOVA and Tamahane's test were used to compare the number of species and the coverage on the various block sides over the entire study period. Statistical analyses were performed with the SPSS statistical package.

After the biotic survey, specimens from four taxa were collected from each block for chemical analysis: *Aglaophenia pluma* (hydrozoa), serpulids (Polychaeta), *Pinctada radiata* and *Spondylus spinosus* (bivalvia). The block surface was then cleaned from fouling by scraping and a small part of the upper 0.5-cm depth layer was carefully broken and taken for chemical analysis. This layer was chosen for analysis because previous studies had shown changes only at the surface of stabilized blocks (Hockley and van der Sloot, 1991; Collins and Jensen, 1995). The block was then transferred to NBRI for measuring compressive strength (Yegerman and Sikuler, 1987).

The block samples were lyophilized for 48 h, crushed to a fine powder, and then totally digested with a mixture of hydrofluoric acid and aqua-regia, as described in ASTM (1983). A separate digestion was performed in concentrated nitric acid (Hornung *et al.*, 1989) for the determination of Hg. The solutions were analysed for Cd, Pb, Cu, Zn, Mn, Cr, Fe, and Al by atomic absorption spectrophotometry using a Perkin-Elmer 1100 B spectrophotometer equipped with flame and graphite furnace modules. Hg was analysed by cold vapour atomic absorption spectrometry on a Coleman Mercury Analyzer MAS-50. The biota samples were pooled by taxonomic group and block type to obtain sufficient weight for analysis; any adhered block material was carefully removed; and the composite samples were then kept frozen at −20°C until analysis. Of molluscs

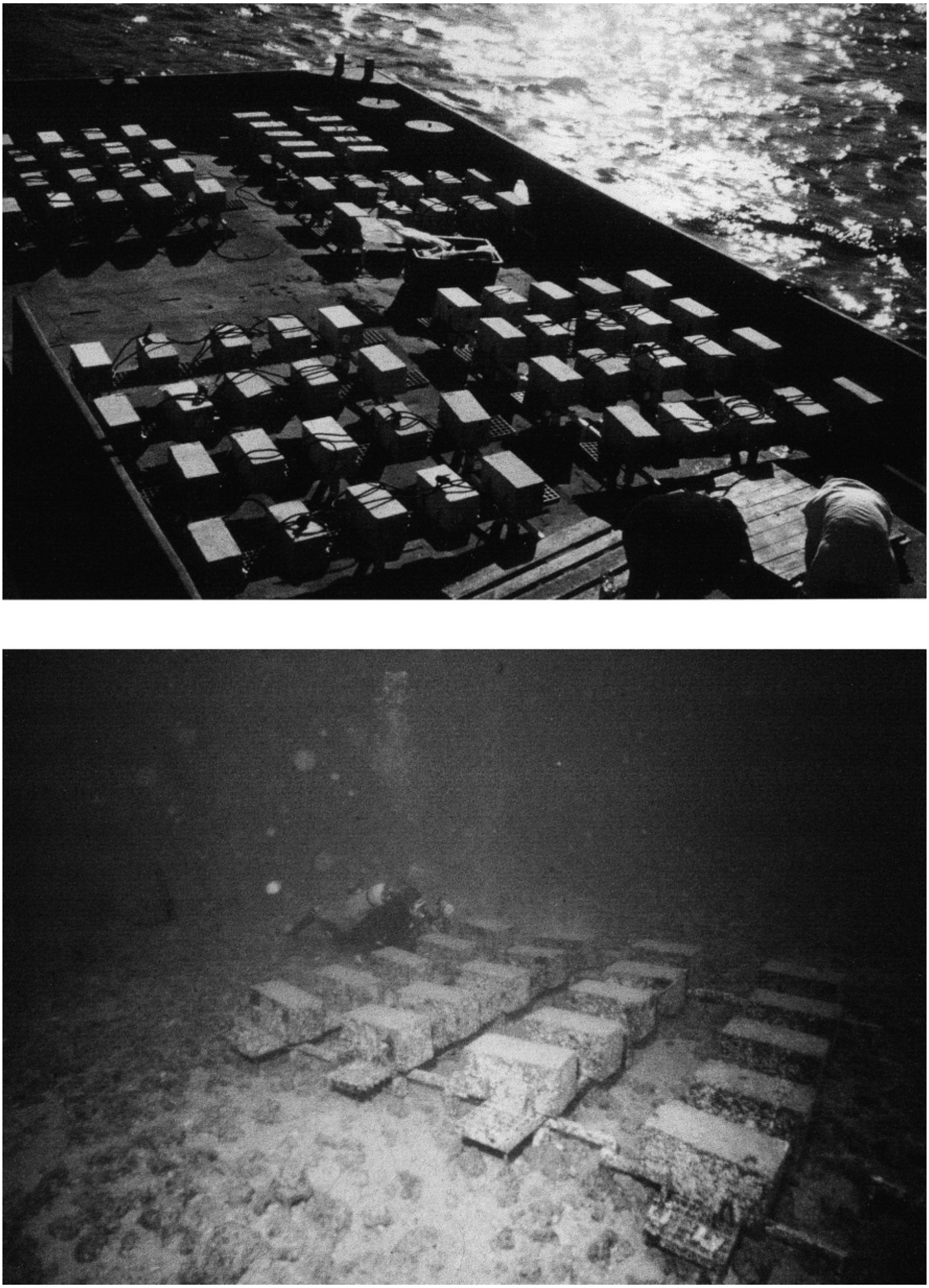

Figure 1. Photograph of the blocks set on the tables on the way to deployment (upper panel) and at the study site (lower panel).

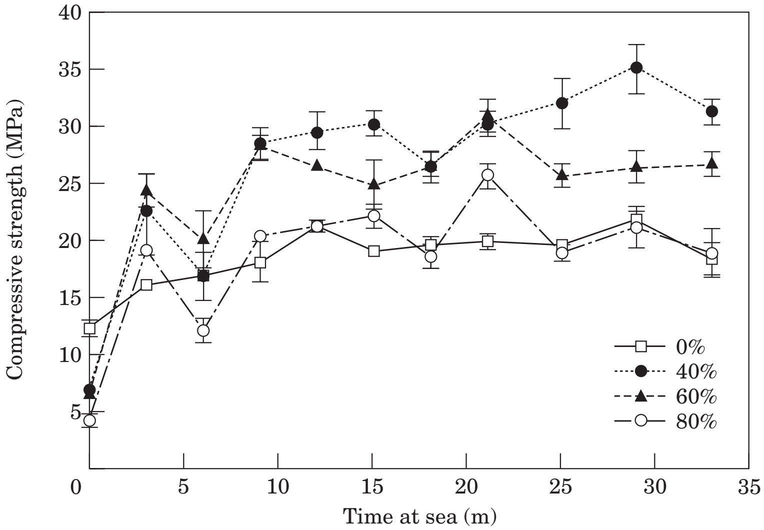

Figure 2. Compressive strength (MPa) of the four blocks types as a function of time at sea.

and serpulids, only the soft tissue was taken for analysis, while hydroids were analysed as a whole. Prior to analysis, the samples were thawed, rinsed, weighed, and then digested with concentrated nitric acid in Uniseal, Teflon-lined, high pressure decomposition vessels, as described by Hornung *et al.* (1989). The solutions were analysed specifically for Cd, Hg, Cu, Zn, Mn, Fe, and Al by the same analytical methods as the blocks.

QC/QA of the results were performed with standard reference materials from the National Institute of Standards and Technology (NIST – Coal Fly Ash-1633a, Estuarine Sediment – 1646, Bovine Liver and Albacore Tuna) and from the National Research Council of Canada (NRCC – DORM-1, DORM-2, and DOLT-1). The standards were digested and analysed in the same manner as the samples during each analytical run. All standard reference materials gave results within 5% of the certified values. Only for cadmium, recovery in Coal Fly Ash-1633 ranged between 71% and 88% and the results were corrected to 100% recovery. Statistical analyses were performed using general linear modelling (GLM) procedures (least squares, t-test, and Mann–Whitney non-parametric test; $p<0.05$).

Results and discussion

Compressive strength

Compressive strength (MPa) clearly increased in all 4 block types during the first 9 months at sea (Figure 2), but remained essentially constant thereafter. The increase was more pronounced in the 40% and 60% blocks than in the 0% and 80% blocks: after 33 months at sea the former were ca. 1.5 times stronger than the latter. CFA-containing blocks showed a four-fold increase in strength (final/initial strength), compared to a 1.5-fold increase in the control blocks. The final compressive strength of all block types was well above 5 MPa, which is considered the minimal strength necessary for the stability of the blocks at sea (Sampaolo and Relini, 1994). Increasing compressive strength with time of immersion has also been reported in other studies (Roethel and Oakley, 1985; Collins *et al.*, 1994; Sampaolo and Relini, 1994; Kuo *et al.*, 1995). Sampaolo and Relini (1994) explained this increase by the pozzolonic activity of the CFA, inducing the formation of stable compounds of hydrated lime with silica and aluminium contained in the ash. Roethel and Oakley (1985) suggested that increasing compressive strength be related to alterations in mineral phase. A similar pattern of rapidly increasing block strength followed by a levelling off has also been noted by Kuo *et al.* (1995) in Taiwan.

Species composition and coverage

Hardly any biota were recorded after three months at sea. The slow development may be explained by the water depth being below the intense influence of wave action and currents, which are known to enhance the dispersal of fouling organisms (Levinton, 1995). Main sessile taxa recorded on the blocks from six months onwards were: filamentous green algae (*Entromorpha* sp.), bryozoa (*Schizoporella errata*, *Thalamoporella gotica* (var. indica), *Mucropetraliella thenardii*, *Parasmittina glomerata*, *Rhynchozoon tubulosum*, *Parasmittina* sp., *Rhynchozoon* sp., *Crisia* sp., *Aetea* sp., *Onychocella marioni*, *Reptadeonella violacea*, *Beania hirtissima*, *Tubilipora* sp.), barnacles (*Balanus trigonus*,

Table 2. Average number of species (n) and percentage coverage (C) with coefficients of variation (cv %) by block side (averaged over all block types and all sampling dates).

	n		C	
Block side	Mean	cv	Mean	cv
Top	3.9	41	7	157
Right	7.9	16	23	61
Left	8.1	21	25	72
Bottom	9.5	22	35	46

B. amphitrite, *B. perforatus*), serpulid polychaeta (*Spirobranchus tetraceros*, *Serpula vermicularis*, *Serpula sf. ancharum*, *Hydroides pseuuncinata pseuuncinata*, *Spirorbis* sp.), hydrozoa (*Aglaophenia pluma*), and bivalves (*Pinctada radiata*, *Spondylus spinosus*). Unidentified sponges were recorded as well.

The effect of CFA percentage on the number of settled species was examined by comparing each side of the blocks among treatments on all sampling dates (multiple two-tailed paired t-test comparisons: n=9). Among the 24 comparisons (6 multiple comparisons among the 4 block types for each of 4 block sides), 22 revealed no significant difference ($p>0.05$). Similar multiple comparisons among percentage coverage of the block sides revealed no significant differences in any of the 24 tested pairs. We therefore conclude that there has been no effect of CFA on either community metric.

In contrast, both number of species and coverage were different when comparing the different block sides over the entire study period (one-way ANOVA). Post hoc Tamahane's tests revealed significant differences among all sides ($p<0.05$), with the exception of the left and right sides, which were similar (Table 2).

Total coverage depended more on block side than on treatment. Bryozoa were the dominant group present, followed by barnacles. Serpulids were also common, especially in the lower, shaded portions of the blocks. Coverage with biota varied seasonally. These variations were largest on the top side of the blocks and smallest on the bottom side. Species composition varied seasonally. In addition, there was temporal succession of certain taxa (e.g. among bivalves, *S. spinosus* appeared after *P. radiata*). Algae dominated the illuminated top side, but total coverage was considerably lower than on the other sides during most samplings. This suggests that the algae competed with or prevented the development of other taxa. In the relatively clear water of the southeastern Mediterranean, the amount of light is usually sufficient throughout the year, even at a depth of 18.5 m, to enable algal growth when proper substrate is available. Only at the beginning of winter 1997–1998 (after 12 months at sea), was algal cover reduced and coverage by other taxonomic groups increased. The top side generally showed the greatest fluctuations in all biological aspects recorded, which may be explained by its exposure to greater changes in environmental factors, especially illumination.

Coverage by Serpulids was at maximum on the bottom side, as expected, because these species prefer shaded sites. The relative stability in number of species and total coverage on the bottom side throughout the study may be attributed to the low and relatively constant level of illumination. Bryozoa dominated the lateral sides and their coverage was usually poorer in winter than in summer.

Metal composition of block surface

The concentrations of trace elements in surface material were proportional to the amount of CFA in the mixture (Table 3). Statistical analysis showed almost no significant changes in composition with time at sea. Only Pb concentrations were significantly lower after 21 months of immersion than the initial values in all block types ($p<0.01$ for 80% CFA and $p<0.001$ for the other types). After 33 months, more changes were noted, in addition

Table 3. Mean (m) heavy metal concentration (ppm; weight % for Fe and Al) and coefficient of variation (cv %) by block type and in CFA as used in their preparation (n=22). In case final concentrations (after 25, 29, and 33 months) differed significantly from initial concentration (after 0, 3, and 6 months), the former are presented in parentheses and the latter in italics (n=6).

	Hg	Cd	Cu	Zn	Cr	Pb	Mn	Fe	Al
% CFA				(ppm)				(wt%)	
100 m	0.29	0.64	83	83	172	138	311	3.21	14.9
cv	3	8	4	1	2	10	1	2	2
80 m	0.14	0.36	49	72	98	*66* (45)	*254* (291)	2.24	7.9
cv	26	39	8	25	19	*34* (10)	*9* (2)	8	13
60 m	0.12	*0.36* (0.26)	41	63	82	*51* (31)	237	*1.94* (1.67)	*7.2* (5.7)
cv	33	*8* (23)	10	22	16	*40* (13)	8	*4* (8)	*15* (12)
40 m	0.071	0.23	30	48	59	*35* (24)	191	*1.56* (1.11)	*5.1* (3.5)
cv	37	40	18	35	14	*10* (23)	7	*15* (9)	*30* (5)
0 m	0.014	0.15	14	39	24	*32* (6.0)	*115* (134)	0.54	0.96
cv	46	91	29	51	21	*35* (8)	*12* (11)	28	18

to a continuing decrease in Pb concentrations. Fe and Al had decreased in the 40% and 60% blocks ($p<0.05$), Cd in the 60% blocks ($p=0.005$), and Mn had increased in the 0% and 80% blocks ($p<0.01$). This suggests that long-term processes are involved and that the steady state may not have been reached after 3 years of deployment.

Although this has been the first study to check metal availability from stabilized Israeli CFA to the marine environment, earlier studies have found leaching of trace metal from unconsolidated CFA (Kress, 1993; Shoam-Frider, 1997; Kress and Herut, 1998). Comparison of the results obtained with consolidated and unconsolidated CFA shows some differences: (a) the time scale to detect leaching from unconsolidated CFA is much shorter than for stabilized blocks; (b) changes in main element composition were larger in stabilized blocks than in unconsolidated CFA, while the latter showed wider changes in trace metal composition; (c) the consolidation process stabilized the CFA and prevented leaching from the blocks, in particular of cadmium, while Cd leached from unconsolidated CFA (Cd is a trace element of particular environmental concern and is cited specifically in the Israeli legislature).

Some of the changes in block composition reported are in agreement with earlier work. For example, van der Sloot *et al.* (1985) found a decrease in Zn and Pb in solidified coal ash after 1.5 years at sea and some Mn enrichment. Surficial Mn enrichment was also found by Roethel and Oakley (1985), who suggested local precipitation of non-soluble Mn species owing to pH and oxygen changes in the micro-environment at the block surface that were caused by Ca dissolution. A decrease in Pb was found also by Labotka *et al.* (1985) in blocks of coal ash and flue-gas desulfurization waste. They showed also that Al-containing minerals – mullite and ettringite – dissolved from the block surface. This might also explain the decrease in Al observed here. Collins *et al.* (1994) and Collins and Jensen (1995) examined CFA blocks from an experimental reef in the UK after 2 and 4 years immersion at sea. They found no significant temporal changes in heavy metal concentrations except for replacement of Ca by Mg. There were some indications of surface loss of Cd and enrichment of Mn and Cr. Sampaolo and Relini (1994) found a decrease in Al and Cr and an increase in Mn (among others) in coal waste blocks in laboratory experiments. When the blocks were immersed in tanks with flowing seawater, no significant changes were identified. Kuo *et al.* (1995) did not detect leaching of any of the six elements monitored by them.

Trace metal in sessile biota

The concentrations of trace elements in sessile biota were measured starting from 9 months' immersion, when sufficient quantities had become available for chemical analysis (Table 4). Mercury was below the detection limit (0.005 μg g^{-1} wet wt) in all samples. Possible changes in trace metals in biota were checked in two ways: (a) as a function of immersion time within block type, and (b) as a function of block type at the same immersion time.

Table 4. Mean trace metal concentrations (m, μg g^{-1} wet weight; Hg was below detection limit) and coefficient of variation (cv %) by taxon (n: number of observations; only results that were not statistically different have been incorporated).

	Cd	Cu	Zn	Fe	Mn	Al
Serpulidae						
m	2.04	5.78	227	445	22.6	511
cv	50	56	33	52	75	54
n	60	60	60	60	60	60
Spondylus spinosus						
m	1.14	8.70	20.8	103	18.4	85.1
cv	22	27	95	21	75	24
n	20	20	20	15	15	15
Pinctada radiata						
m	1.15	7.54	205	270	17.8	290
cv	48	69	67	63	53	72
n	39	18	40	30	41	30
Aglaophenia pluma						
m	0.47	17.1	66.7	2939	91.4	3445
cv	62	69	77	53	54	50
n	44	12	25	11	49	23

Changes in trace metal concentrations in Serpulids were not significant, neither as a function of block type nor of immersion time. In the two mollusc species, there were almost no significant changes and those detected did not show a systematic trend or pattern. In *P. radiata*, Cu decreased with time for 0% and 60%, Fe in the 40% and Al in 60% blocks, while for *S. spinosus* significantly lower Fe and Al concentrations were measured for 80% blocks and higher Mn concentrations for 0% blocks.

The hydroid *Aglaophenia pluma* showed more significant changes: Cu and Fe decreased with time in 0%, 40%, and 60%, Zn and Cr in 40% and 60% and Al in 0% and 60% blocks. The concentrations decreased with time, which is opposite to the trend expected if bioaccumulation has occurred. Because we did not estimate the lifespan of the sampled biota, the observed changes in composition may be due to changes in physiological state. Collins and Jensen (1995) found similar trace metal contents in hydroids sampled from blocks after 4 years at sea, but no differences between specimens collected from the blocks with or without CFA.

Conclusion

Pickering (1996), in her review on scientific and legal suitability of using CFA in the marine environment, concluded that the balance of scientific evidence lies in favour of the physical and environmental integrity of stabilized blocks. However, although the scientific evidence points to environmentally safe usage, she suggests that future research will need to address still existing concerns of policy-makers and legislators. Our results show that, at least in the short term of 2 to 3 years, there would be no environmental hazard to utilize Israeli CFA in the construction of block units for artificial reefs. Compressive strength increased with time at sea, no effects were detected on number of species and overall coverage, and only few changes in trace metal composition of both blocks and sessile biota were detected. However, artificial reefs are deployed at sea for much longer than 33 months and the integrity of block material and potential long-term effects on the biota should be investigated further.

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