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Partial replacement of cement for waste aggregates in concrete coastal and marine infrastructure: a foundation for ecological enhancement?

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Abstract

The effects of climate change and an expanding human population are driving the need for the expansion of coastal and marine infrastructure (CMI), the development of which is introducing hard substrate into the marine environment on a previously unseen scale. Whilst the majority of previous research has focussed on how physical features affect intertidal macrobiotic communities, this study considered the effects of differences in the chemical composition of concrete on subtidal biofilm and macrobiotic communities. Two commonly used cement replacements, pulverised fly ash (PFA) and ground granulated blast-furnace slag (GGBS), were used in a combination of proportions to assess how concrete tiles with differing surface chemistries affect development of early successional stages of marine biofouling communities. Controlled leaching experiments showed that although total metal leaching varied considerably between tile type, tiles containing GGBS resulted in statistically lower amounts of metal released compared with tiles containing PFA. Concrete treatment had no effect on the percentage cover or richness of diatoms, but there were significant increases in both over the duration of the experiment. Concrete treatments containing GGBS had a lower richness of native macro-fouling species compared to the control, but there was no significant difference in non-native species richness among treatments. Results suggest

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that different components can be used to alter the surface chemistry of concrete to further enhance the ecological value of CMI more than physical features can achieve alone.

Key words: Marine, concrete, ecology, biodiversity, water quality, elements

1. Introduction

1.1 Expansion of coastal and marine infrastructure (CMI)

With the pressures of climate change and many of the world's population living on or near the coast (Small and Nicholls, 2003), there is growing demand for development of the marine and coastal environment (Nicholls and Kebede, 2012). Furthermore, with the introduction of artificial hard substrata into the marine environment on a large scale (*sensu* "ocean sprawl"), there is a pressing need to determine the effects that this is having on the biofouling communities that colonise them, their ecology and impacts on the wider marine environment. The recent surge of interest in the ecology of the built environment has yielded a wealth of research describing the impacts of these structures on the receiving environment (Dafforn et al. 2015, Bishop et al. 2017), the fundamental differences in both the structure and functioning of artificial habitats compared to their natural analogues (see Firth et al. 2016a for review) and changing attitudes of humans to hard artificial structures (Evans et al. 2017; Morris et al. 2015; Scyphers et al. 2015). There is a growing consensus that artificial structures are characterised by lower diversity and abundance of native species (Aguilera et al. 2014; Burt et al. 2009; Chapman, 2006; Firth et al. 2013) and are known to support high diversity and abundance of non-native and opportunistic species (e.g. Bulleri and Airolidi, 2005; Firth et al. 2011, 2015; Mineur et al. 2012).

The nature of the material used in CMI can influence the ecological attributes (e.g. biodiversity, community composition) of organisms that settle on it. This is largely due to variations in habitat heterogeneity at a range of spatial scales (Anderson and Underwood, 1994; Chapman and Underwood, 2011; Connell, 2000; Coombes et al. 2015; Firth et al. 2013; Harlin and Lindbergh, 1977; Moschella et al. 2005), but is also linked to chemical cues (Anderson, 1996; Neo et al. 2009) and even colour (Pomerat and Weiss, 1946; Satheesh and Wesley, 2010). Because artificial environments generally have lower native species richness and are more likely to be dominated by opportunistic or non-native species, there are opportunities to enhance CMI for conservation purposes and ecosystem services (Chapman and Underwood, 2011; Dafforn et al. 2015; Firth et al. 2016a; Seaman, 2007). To date, the majority of research has focussed on the physical properties of artificial structures, but knowledge gaps exist of other factors that could be driving the differences between the

ecology of natural and artificial marine environments; for instance, substrate surface chemistry (but see Nandakumar et al. 2003; Perkol-Finkel and Sella, 2015; Sella and Perkol-Finkel, 2015).

1.2 Replacing cement with waste aggregates in coastal and marine infrastructure

When hard substrata, artificial or otherwise, are introduced into the marine environment, biofilms (formed of benthic microalgae, bacteria and other micro-organisms embedded in a matrix of extracellular polymeric substances (EPS)) are the first colonisers. Previous research has shown that biofilm succession and species composition can be affected by fine-scale substratum roughness (Sweat and Johnson, 2013), environmental pollution (Sanz-Lazaro et al. 2015) and surface chemistry (Nandakumar et al. 2003). Marine biofilms are known to interact directly with macro-fouling organisms (Salta et al. 2013) and differences in biofilm community structure may influence their attachment (Ank et al. 2009).

Portland cement is the major construction material used globally in artificial structures, often making up over half of coastal and marine developments (Kampa and Laaser, 2009). Although biotic communities can and do colonise concrete substrates (e.g. Firth et al. 2016b; Griffin et al. 2010), concrete is considered a poor substrate material for biotic recruitment due to its high surface alkalinity (pH ~13) and the fact that it can contain toxic metals, which can interfere with larval settlement (Nandakumar et al. 2003), and affect the emergent community structure and its functioning (Perkol-Finkel and Sella, 2015; Sella and Perkol-Finkel, 2015). Typically, concrete has four main ingredients: coarse aggregate (e.g. gravel), fine aggregate (usually sand), cement and water; although its properties can be amended to improve strength or resistance to sulphate and chloride attack (Snelson and Kinuthia, 2010). This can be achieved by changing the types and proportions of ingredients, as well as by using additional ingredients such as silica fume, pulverised fly ash (PFA), ground granulated blast-furnace slag (GGBS), carbon fibres (Graham et al. 2013) and hemp fibres (Dennis et al. in press). Not only do these materials change the physical properties of concrete, but they can also inherently change its chemical composition. Cement production is extremely energetically expensive, accounting for 8% of global CO₂ emissions (Achternbosch et al. 2011). There is therefore an incentive to use cement replacements, not only as it reduces the carbon footprint of the end product (concrete), but also uses waste products that may otherwise go to landfill (Bignozzi, 2011).

PFA is a waste product from burning coal, removed from flue gases by electrostatic precipitators. It is well reported that the addition of fly ash into cement mixes can greatly improve durability, resistance to sulphate attack and chloride penetration, and reduce the likelihood of leaching effects (e.g. Chalee et al. 2010; Thomas and Matthews, 2004). GGBS is a by-product of the steel industry made by grounding iron slag into a fine powder, which when used as a (partial) replacement for cement, can provide resistance to sulphate attack without any loss of durability or compressive strength (Pavia and Condren, 2008). The use of PFA and GGBS as replacements for cement in concrete is well established. GGBS can be used as a direct replacement for Portland cement, on a one-to-one basis by weight, with replacement levels of between 30% and 85% reported. Typically, 40 to 50% replacement is most common in order to maintain structural integrity. PFA replaces a certain percentage of Portland cement, usually between 6 to 35% according to British standard EN 197-1: 2011 (British Standards Institute, 2011). Both replacements are primarily composed of calcium oxide, and silicate and aluminate glass spheres. As such, they are highly alkaline (pH > 9) and contain relatively high concentrations of trace metals (Table 2, Mullauer et al. 2015) such that while the use of waste products in concrete is positive from a sustainability point of view, these concretes may not be as environmentally sound when it comes to enhancing ecological value in terms of marine conservation, biodiversity and ecosystem services.

1.3 Chemical leaching from coastal and marine infrastructure

Previous studies have shown that metal leaching can occur at the outer layer of the concrete during the first 30 days of immersion (Shi and Kan, 2009), but some metals can leach in greater concentrations from PFA and GGBS over longer time periods (Jang et al. 2015). The general consensus in the literature appears to be that metals within cement and fly ash can leach out of concrete, albeit at relatively low concentrations owing to cement hydrates immobilising the majority of the metals, particularly in the core, with only the outer surface leading to the dissolution of metals into the aqueous phase. Despite this evidence, it is apparent that leaching of metals still occurs, and in some cases, exceeds the standards set for protecting marine species and the environment.

The majority of previous research on cement replacements has focused on the chemical properties of cement replacements, but few studies have investigated the ecological effects

(Izquierdo et al. 2009; Jang et al. 2015; Müllauer et al. 2015). Here, the leaching of metals and the effects of the chemical nature of concrete on colonising communities were investigated using two cement replacements (PFA and GGBS). This research seeks to open up new opportunities for research into alternative cement replacements and their use in enhancing the ecological value of biofouling communities. Using a combination of laboratory and field experiments, we aimed to determine: (1) the metal composition of the concretes and its variability; (2) the significance of the leaching of metals from cement replacements into seawater; (3) the impacts of cement replacements on colonising biofilms in terms of species richness and cover; (4) the effects of cement replacements on colonising macrobiota, with particular reference to differential responses of native and non-native species.

2. Materials and Methods

2.1 Study site

Fieldwork was carried out at the Plymouth University Marine Station at Queen Anne's Battery marina in Plymouth Sound at the mouth of the Tamar Estuary (50.3648° N, 4.1298° W). Queen Anne's Battery is a sheltered marina located in a busy shipping area for recreational boating, commercial fishing as well as international commercial transport of fuel and bulk aggregates. The colonising communities on the marina pontoons (floating docks) were characterised by ascidians, bryozoans and macro-algae, including a high abundance of non-native species (Arenas et al. 2006; Bishop et al. 2013). Due to its importance as an international shipping port with a long history of marine biological research, Plymouth Sound is well known for being the site of many first records of non-native species (Knights et al. 2016). Salinities over the course of the sampling period (summer) vary between 28 and 30 ppt, pH between 8.0 and 8.4, and temperature between 16 and 18°C (Langston et al. 2003). These conditions are typical of temperate coastal waters of equivalent northern or southern latitudes, which suggests wide applicability of the data to other sites worldwide.

2.2 Experimental design and concrete production

Our goal was to devise an experiment that provided the opportunity to observe potential differences in chemical leaching and species recruitment between concrete mixtures, whilst being realistic in terms of the mixtures used commercially in construction, and therefore the physical integrity required for their engineering application. As we wished to achieve

relatively high replication for the leaching trials, the number of concrete mixtures used was limited to four (Table 1), but with recognition that many more cement replacement combinations could be tested.

In this experiment a replacement of 24% cement for GGBS/PFA (direct replacement-by-weight) was chosen. While a relatively low level of replacement for GGBS, this is toward the middle to higher-end level of replacement for PFA. Given that one of the mixtures contains both PFA and GGBS, testing of any chemical interactions led to a replacement of 48% cement by PFA and GGBS, but still within the range of percent replacement by either GGBS or PFA used in industry (see above). Using the replacement percentages meant that the metal composition of the base components would be sufficiently differentiated to allow the analytical methodologies to determine any differences in leaching behaviours between concrete types.

Concrete tiles were constructed using four different mixtures. We refer to the different mixtures as 'types'. Standard 'control' concrete was made using a mixture of standard high strength cement (CEM-1), sand, crushed granite (4-10 mm) and water. The three other concrete types had cement partially replaced by pulverised fly ash (PFA), ground granulated blast slag (GGBS), or a mixture of both PFA and GGBS (Mixed; see Table 1 for details).

Tiles of two different sizes (25 x 25 x 5 cm; and 2 x 2 x 1.5 cm) were cast in silicone trays to aid mould release and to negate the use of a release agent, then covered in a polyethylene sheet and allowed to cure for 2-wk (Zemajtis, 2016). The larger-sized tiles were used for the chemical analyses whilst the smaller tiles were used for biological analyses. The smaller size was specifically chosen to allow tiles to be placed in an electron microscope for biofilm analysis.

Table 1. Description of concrete treatment compositions. Percentage of ingredients used to create the different concrete types expressed as a percentage by-weight. Note that 4% PFA/GGBS corresponds to by-weight ~24% (4/17) replacement of cement.

Concrete Type	Cement	Sand	Crushed Granite	Water	PFA	GGBS
Control	17%	27%	47%	9%	0%	0%

PFA	13%	27%	47%	9%	4%	0%
GGBS	13%	27%	47%	9%	0%	4%
Mixed	9%	27%	47%	9%	4%	4%

2.3 Chemical testing

To minimise the possibility of contamination of the materials and samples with trace metals, all equipment used for collecting samples was washed in 10% nitric acid and rinsed 3-5 times with deionised water (Milli-Q; >18 MΩ.cm, Merck Millipore, USA) prior to use.

2.3.1 Media Aqua Regia digestion of the concrete components

In order to determine the metal content of the base components of the concrete mixes used, samples (5g) of the individual concrete components (GGBS, PFA, granite, sand, cement) were placed into 250ml glass beakers. Owing to its size (4-10mm), the aggregate was ground down into a powder using a mortar and pestle. 70ml of nitric acid (Sigma-Aldrich S.G.) and 30ml of hydrochloric acid (Sigma-Aldrich S.G 1.18) was added and left to stand for 60 min. Samples that had not fully dissolved had 5ml Aqua Regia solution added and were placed on a hot plate at 90°C and allowed to simmer for 60 min until fully dissolved. The solution was then filtered through a Whatman cellulose acetate membrane into volumetric flasks and made up to a known volume using 2% nitric acid.

2.3.2 ICP-MS determination

All acid digested samples were determined for elemental composition using a Thermo Scientific X-Series 2 Inductively Coupled Plasma – Mass Spectrometer (ICP-MS). Standards for seawater analysis were made using CPI International multi-element quality control standard (P/N 4400-013) and Romil Mercury element reference solution, diluted to working ranges using Milli-Q water. Control samples and calibrations were run at the beginning and end of each batch of analysis and filter and acid blanks determined to check for sample contamination. Recovery was compared against independent control samples and were 107 ±10% for Cr, 106 ±8% for Zn, 105 ±11% for Mo and 105 ±10% for Ba. Limits of detection based on using 3 times the standard deviation of the blank were 0.01, 0.09, 0.25, 0.11, 0.16, 0.16 and 0.01 µg/l, 0.16 for Cr, Cu, Zn, Se, Mo, Ba and Pb respectively.

2.3.3 Chemical leaching tests

It was assumed that there was a certain degree of heterogeneity on the surface of each type of tile exposed to seawater for any given concrete mix. Consequently, all tests were undertaken using five replicates for each treatment. Individual large concrete tiles were fully submerged in tanks of seawater and 125ml water samples were collected at fixed time points from 5 cm depth at the centre of the well-mixed tank. Water samples were stored in HDPE bottles (Nalgene). After 18 h immersion, the seawater in each tank was replaced with fresh seawater to ensure leaching rates were not affected by increased chemical concentrations within a tank that might result in reduced leaching due to a change in concentration gradient. In total, tiles were immersed for 1296 h (54 days). The cumulative chemical concentration leached into the water was calculated over time to: (i) determine total chemical concentration leached from each tile, and (ii) to identify the point of asymptote, i.e. when no further chemicals were leached from the tiles. At each time interval, measurements of pH, salinity and temperature were also taken using a YSI 63-25 multi-parameter probe.

All water samples were filtered through a 0.45µm polycarbonate membrane previously cleaned with 30% hydrochloric acid for 24 hours and rinsed 3-5 times with Milli-Q water (Merck Millipore, USA). After filtration, 1ml of seawater was decanted into a 15ml polyethylene centrifuge tube and 9 ml of 2% nitric acid added as a matrix diluent and preservative. Chemical concentrations were then determined using ICP-MS determination techniques as outlined above.

2.4 Study of colonising biota

To study the growth of biofouling assemblages on the submerged tiles, small concrete tiles were attached to wooden beams using cable ties and hung from pontoons at a depth of 0.5m for 49 days (28/6/16 to 16/8/16). Tiles were arranged randomly and orientated so that the front faces of the tiles were vertical.

2.4.1. Assessment of colonising biofilms

Colonising biofilms were assessed by collecting fifteen replicate samples from each of the four treatments (i.e. concrete types) at weekly intervals over 4 weeks (05/07/2016 to 26/07/2016). Each sample was fixed and preserved in 5% glutaraldehyde solution, using seawater as a buffer, and kept refrigerated. Samples were washed and then air-dried for 7 days before imaging using low-vacuum scanning electron microscopy (LV-SEM; JEOL

6110). LV-SEM negates the need for sample preparation by spatter-coating; a process required for high-vacuum SEM. From these images, all diatoms present were identified to genus and percentage cover estimated using a 10 x 10 virtual grid quadrat (500 x 500 μ m). Here, given the expertise available, we focused on diatoms but acknowledge that future studies should consider all microorganisms in the biofilm.

2.4.2. Assessment of colonising macro-fouling communities

Colonising macro-fouling communities were determined using five replicates collected from each of the four concrete mixture types after seven weeks and transported to the lab where they were kept in aerated seawater aquaria. In the laboratory, all macro-organisms on the front face of the tiles were identified to species and presence/absence recorded using classical taxonomic methods.

2.5 Statistical analyses

2.5.1 Chemical analysis

Change in the combination of chemicals leached from tiles of different construction materials (Table 1) were compared using two analyses. Firstly, the 'community' of chemicals leached by tiles over time were compared using typical ecological tools (i.e. PERMANOVA, Multidimensional scaling (nMDS) and diversity indices), where the 'chemicals' are considered the 'species' and the chemical concentration the 'species abundance'. Chemical identity and concentration matrices were compared using PERMANOVA based on 9999 unrestricted permutations (Anderson, 2001). Chemical community dissimilarity (see Oksanen et al. 2013) was calculated using Euclidean distance (see Clarke and Warwick, 1994) and plotted using nMDS. Environmental fitting using the 'envfit' function (vegan package, R Core Team, 2016) was also used to overlay (1) a vector of the effect of time (a continuous variable) on dissimilarity, and (2) to determine the centroid (average) location of communities in relation to tile type (a categorical variable).

A univariate comparison of chemical leaching was also undertaken by reducing the community of chemicals into a univariate diversity index (i.e. Shannon-Wiener Index [H']) to test for differences in the evenness (proportional contribution to the total abundance) of chemicals leached from each tile type. One-way ANOVA was used to test for differences in H' values between each tile type, and post-hoc SNK tests used to show pairwise differences

between groups. Data were normal distributed but variances heterogeneous and were therefore log-transformed in order to remove heterogeneity.

The leaching of individual chemicals over time was assessed using LOESS curve fitting (local regression in the R package 'ggplot2') due to the temporal autocorrelation inherent in the data over time. Individual concentrations were log-transformed and assessed using goodness of fit (R^2).

2.5.2 *Biological communities*

Two-way analysis of variance (ANOVA) was used to determine whether there was a significant effect of treatment (concrete type) on biofilm percentage cover and richness using the fixed factors: 'type' (four levels, fixed) and 'time' (4 levels (weeks), random, orthogonal).

One-way ANOVA was used to analyse the effect of concrete type on macro-fouling species richness after seven weeks using the fixed factor concrete 'type' (four levels, fixed). Data were analysed separately for native and non-native species. One-way ANOVA was also used to test the effect of concrete type on the relative proportion of non-native species. Post-hoc SNK tests were used to show pairwise differences between groups. GMAV version 5 for windows (Underwood & Chapman, 1998) was used for all analyses.

PERMANOVA was used to test for differences in multivariate native and non-native species compositions among concrete types, based on 9999 unrestricted permutations of raw presence/absence data (Anderson, 2001). Percentage contributions of individual taxa and functional groups to dissimilarity between communities were calculated using SIMPER (Clarke, 1993). SIMPER analysis in the PRIMER package was used to assess which species were most influential in causing similarity among plots within treatments and dissimilarity among different treatments (Clarke and Warwick, 1994).

3. Results

3.1 Metal composition of the tiles

Metal concentrations in the individual components of the concrete are provided in Table 2a. The sand and granite components contain relatively low acid-extractable metal concentrations, reflecting their geological origins (high quartz content) and relatively small surface area available to leach and/or desorb metal. The cement, PFA and GGBS, however, have elevated concentrations for certain elements owing to their finer grain size providing a larger surface area to leach/desorb metals and also their more varied and metalliferous source material. Cement itself exhibited the highest levels of chromium and copper, with PFA having greatest quantities of nickel, arsenic, molybdenum, cadmium, mercury, thallium and lead; GGBS exhibited the highest concentrations of zinc and barium. These measured concentrations are in line with those reported previously (Brigden and Santillo, 2002; Ilyushechkin et al. 2012; Moreno et al. 2005; Yu et al. 2005). Estimated combined concentrations of metal within each type of tile was calculated (Table 2b) based on the composition of the tile type taken from Table 1 and multiplied by the metal content in the individual constituents. Although there were significant variations in the concentrations of elements present in the individual components owing to the replacement being only up to 8% by weight, the combined estimated concentrations in the final concrete mix do not vary dramatically. Even then, only for Ba, Mo and Ni does the variation between tile types reach a factor of two (Table 2b).

Table 2. Comparison of the mean metal concentrations in (a) the individual concrete components and (b) in the four treatment types. (c) EQS = Environmental Quality Standard each metal. Values in bold represent those that are above EQS. * = Highest value for the comparison among either the individual components or among treatments. SD = Standard deviation.

(a)		Concentration (mg/kg)										
		Cr	Ni	Cu	Zn	As	Mo	Cd	Ba	Hg	Tl	Pb
Cement	Mean	41.6*	17.9	65.5*	45.9	9.92	1.19	0.31	129	0.04	<0.01	27.8
	SD	0.6	1.94	1.62	0.62	10.54	0.11	0.05	0.009	1.52	n/a	0.0003
Granite	Mean	0.17	0.12	2.34	1.25	0.62	0.01	0.01	3.3	0.02	0.06	1.2
	SD	0.0007	0.0019	0.0782	0.0573	0.0198	0.0117	0.0017	0.0002	0.099	0.0006	0.0024
Sand	Mean	0.14	0.03	1.13	1.13	0.67	<0.01 ⁵	0.01	7.1	0.02	0.06	0.76
	SD											

	SD	0.0064	0.0008	0.0538	0.0633	0.0412	n/a	0.0006	0.0011	0.2219	0.0005	0.0033
PFA	Mean	32.1	47.7*	39	50.6	23.1*	3.92*	0.33*	180	0.08*	0.19*	50.2*
	SD	0.3	0.3	0.38	1.53	0.65	0.13	0.11	0.008	5.51	0.0012	0.0049
GGBS	Mean	26.5	2.04	2.04	147.5*	10.2	<0.01 ⁵	0.07	603*	0.01	0.01	8.2
	SD	0.27	1.56	0.5	2.99	5.63	n/a	0.009	0.009	9.61	0.003	0.001
(b)												
Control	Mean	7.2*	3.1	12.5*	8.7	2.2	0.21	0.06*	25.4	0.022	0.053	5.5
PFA	Mean	6.8	4.3*	11.5	8.9	2.7*	0.32*	0.06*	27.4	0.023*	0.059*	6.4*
GGBS	Mean	6.6	2.5	10	12.8	2.2	0.16	0.05	44.4	0.02	0.051	4.7
Mixed	Mean	6.2	3.7	8.9	12.9*	2.7	0.27	0.05	46.4*	0.022	0.057	5.6
(c)												
EQS ¹		0.6 ² (32)	8.6 ⁴ (34)	3.76 ^{2,3}	7.92	252	n/a	0.24	n/a	(0.07) ⁴	n/a	1.3 ⁴ (14)

¹ Environmental Quality Standard; ²WFD, (2015); ³ Assumes DOC < 1 mg/l; ⁴EU, (2013) ; ⁵ For the purpose of calculations < values converted to half the LOD. All EQS as annual averages unless in brackets denoting maximum admissible concentrations.

3.2 Metal leaching from the tiles

There were significant differences in the profiles of the elements and their concentrations leached from the different treatments over time (Table 3a, Fig. 1a). While differences in chemical composition were apparent, treatment only accounted for 6% of the variability, whereas time accounted for 38% of the variability (Table 3a, R² values). Comparison of chemical composition using a diversity index (Shannon-Wiener) better revealed differences in chemical leaching between treatments (Fig. 1b). The PFA treatment (Type 2) exhibited significantly greater log H' chemical compositions than GGBS and Mixed treatments respectively, indicating increased leaching (Fig. 1b). The GGBS treatment had the lowest H' values, indicating reduced leaching, although this reduction in H' was counteracted in the Mixed treatment; although this experimental design cannot be used disentangle the effect of introduced PFA from a reduced amount of cement in the mixture. Control concrete H' values were statistically the same as tiles including both GGBS and PFA (Mixed treatment; p > 0.05), but higher than H' values in treatments with just GGBS (Type 3).

There were differences in the concentration of chemicals leached from the tiles (Fig. 2) over time. In all instances, asymptote was reached (no further leaching) after a total of 250 h of

immersion for all chemicals. Zinc (Zn) was the most abundant chemical and lead (Pb) the least abundant chemical leached from the tiles (Fig. 2).

Table 2. (a) PERMANOVA comparing the chemical types and concentrations leached Control, PFA, GGBS and Mixed tiles. Significant P-values are highlighted in bold. (b) ANOVA comparing Shannon diversity of chemicals leached from tiles of different type (as described in (a) above).

a).

Source	Df	MS	F	R2	P
Type	3	518.0	13.58	0.06	<0.001
Time	1	9727.1	255.04	0.38	<0.001
Type x Time	3	67.3	1.77	0.008	0.151
Residuals	371	38.1		0.55	

b).

Source	Df	MS	F	P
Type	3	0.546	12.25	<0.001
Residuals	375	0.045

377 Figure 1. (a) nMDS plot of dissimilarity of chemical composition (identity and concentration)
378 leached from different tile types over time. Significant vector (time, $p < 0.001$, $R^2 = 0.56$) and
379 the centroid (average location) of each tile type (Type 1 – 4) shown in bold lettering ($p <$
380 0.05 , $R^2 = 0.03$) are shown following environmental fitting. Stress = 0.01. (b) log mean
381 Shannon diversity ($H' \pm S.E$) of chemicals leached from tiles of different composition. Letters
382 denote statistical groupings; groups identified by post-hoc SNK tests; groups that do not
383 share a letter are significantly different from one another ($p < 0.05$).
384

Figure 2. Cumulative concentration of seven chemicals (ug/l) leached from tiles over the significant main effect of time (hours of immersion). Data are pooled across all tile types. Local regression (LOESS) lines are fitted and confidence limits (grey shading) are shown. Goodness-of-fit (R^2) values for each LOESS line are shown.

3.3 Effects on colonising biofilms

A total of seven genera of diatom were found to have colonised the tiles (*Thalassiothrix*, *Fragilaria*, *Asterionella*, *Amphiprora*, *Grammatophora*, *Surirella* and *Tabellaria*). Plate 1 shows examples of images obtained from SEM. The ANOVA showed that there was a significant difference between treatments (Table 3), however post-hoc tests failed to identify where these differences were (Fig. 3a). There was no significant difference in biofilm diversity among treatments (Fig. 3b, Table 3), but both biofilm % cover and diversity increased significantly through time as expected (Fig. 3c,d, Table 3).

Plate 1. Examples of SEM images (x 200 zoom) obtained from control concrete blocks after (a) 1-wk, (b) 2-wk, (c) 3-wk, and (d) 4-wk.

Table 3. ANOVA comparing % cover and richness of biofilm among the four different concrete types across four weeks. Significant P-values are in bold.

Source	df	% cover			Richness		
		MS	F	P	MS	F	P
Type	3	369.35	3.21	0.029	0.35	0.26	0.857
Week	3	2628.15	22.86	0.000	22.15	16.18	0.000
Type x Week	9	125.36	1.09	0.383	0.31	0.23	0.989
Res	64	114.99

Figure 3. Comparison of mean % cover and richness of biofilms across the significant main effects of treatments (a,b, pooled over time) and time (c,d, pooled over treatment) over a 4-week period (n = 20, $\pm$ SE). Letters denote statistical groupings; groups identified by post-hoc SNK tests; groups that do not share a letter are significantly different from one another. Despite ANOVA detecting a significant effect of treatment for biofilm % cover (a), post-hoc SNK tests failed to detect any significant differences among treatments.

3.4 Effects on colonising subtidal macro-biota

A total of 27 species colonised concrete tiles after 7 weeks (Table S2). These comprised ascidians (10 species), bryozoans (5 species), algae (5 species), amphipods (3 species), sponges, hydroids, annelids and barnacles (1 species each). Five of the 27 species identified were non-native to Britain but common in Plymouth Sound: the bryozoans *Tricellaria inopinata* and *Watersipora subtorquata*, the hydroid *Bugula neritina*, the ascidian *Botrylloides violaceus* and the barnacle *Austrominius modestus*.

Treatment had a significant effect on native species richness but no significant effect on either non-native species richness or the proportion of non-native species per treatment (Figure 4, Table 4). Control tiles had the highest mean native species richness (9.2) whilst mixed tiles had the lowest (7.4). Control tiles had significantly greater native species richness than both GGBS and mixed, but were not significantly different to PFA.

There was a significant difference in native species composition among treatments but no significant difference was detected for non-native species (Fig. 7, Table 5). The native macro-fouling assemblages associated with the controls exhibited the highest average similarity (68.5%); Mixed exhibited the lowest average similarity (57.9%) and PFA and GGBS were in between (61.3% and 61.4% respectively). This is reflected in the clustering of the shapes for the controls and dispersed shapes for Mixed in Figure 5. SIMPER analysis revealed that there were greater numbers of taxa associated with controls (the amphipod, *Jassa marmorata*, the bryozoan, *Cradoscrupocelleria reptans*, the alga, *Ceramium rubrum*, the ascidian *Ciona intestinalis*) than the other treatments. The ascidians *Ascidella aspersa* and *Botryllus schlosseri* were more positively associated with PFA and GGBS respectively than the other treatments. Furthermore, two native species were unique to the Control (*Ulva linza* and *Corella parallelogramma*). Non-native species were found on all concrete types, but the invasive barnacle *Austrominius modestus* was unique to GGBS and Mixed treatments.

Table 4. ANOVA comparing mean richness of native and non-native species among the four different concrete types. Significant P-values are in bold.

Source	df	(a) Native richness			(b) Non-native richness			(c) Proportion of non-native species		
		MS	F	P	MS	F	P	MS	F	P
Type	3	8.86	4.83	0.005	0.77	0.75	0.52	0.0086	0.38	0.7692
Res	56	1.83			1.02			0.0229

Figure 4. Comparison (a) mean species richness of native species, (b) mean species richness of non-native species (c) mean proportion of non-native species across the four concrete types after 7 weeks (n = 15, ± SE). Letters denote statistical groupings; groups

identified by post-hoc SNK tests; groups that do not share a letter are significantly different from one another. Grey bars = native species, black bars = non-native species.

Table 5. PERMANOVA comparing native and non-native species compositions among the four different concrete types. Significant P-values are in bold.

Source	df	Native composition			Non-native composition		
		MS	F	P	MS	F	P
Type	3	1776.5	2.16	0.006	0.53	0.52	0.929
Res	56	822.72			1.02

Figure 5. MDS plot of native species assemblage dissimilarity among different concrete types (see legend).

4. Discussion

4.1 Leaching chemistry of the concretes

Although cement replacement material had metal concentrations significantly higher than Portland cement, leaching patterns were very similar reflecting the immobility of the metals present. For example, Se in PFA was almost two orders of magnitude higher but was not detectable in the seawater after leaching periods of up to 672 hours. This is likely a result of the overall composition of the concrete containing relatively low percentages of PFA (24% replacement of cement, but only 4% of the entire concrete mix by weight) and the fact that the metals present are likely to be present as highly insoluble oxide and hydroxide minerals

as a product of the high temperature combustion processes from which they were derived. Leaching chemistry will only be occurring on the surfaces exposed to seawater (van-Jaarsveld et al. 1999). Thus the leaching rate of metals is a function of abundance and distribution of individual metals on the outer surface of the concrete (Shi and Kan, 2009). Despite efforts to ensure homogenous mixing, the potentially uneven distribution of metals within the concrete matrices, especially towards the exterior of the concrete is likely to be a factor in the leaching concentrations of metals observed in this study. In all cases, however, cumulative concentrations plotted against time show an equilibrium being reached at around 250 hours.

Successive immersions of the tiles in fresh seawater were undertaken to ensure that an 'unnatural' equilibrium was not achieved in the immersion tanks, and successive reductions in the concentration of metal leached reflected a combination of surface chemistry, particularly chloride interactions (Perkol-Finkel and Sella, 2015) and natural physico-chemical partitioning processes. The final equilibration concentration tended to reflect the concentration of metal present in the concretes with Zn and Ba the highest and Hg the lowest, with elements such as As, Tl, Cd and Ni being present at below the analytical limits of detection. Based on this study, whether the leached metals are a cause for concern regarding toxicity to colonising organisms is difficult to determine. The tiles exposed to the natural seawater to allow biofilm growth benefit from almost infinite dilution into the surrounding seawater which cannot be replicated within the laboratory environment. There are likely to be elevated metal concentrations at the surface of the tile in contact with the biofilms, but again this is not practically measurable. It was for this reason that a number of water replacements were carried out to establish if fresh seawater interactions results in more or less leaching. The use of tiles submerged in tanks better mimics situations where an enclosed body of seawater is retained between tidal flushing events (e.g. harbours and marinas, where concrete is particularly prevalent). Under these conditions, it is then possible to compare observed leached concentrations with available EQS (Table 2). Concentrations of Zn in the bulk solution did exceed new UK EQS of 7.9 µg/l during individual immersions for all of the treatments reflecting the relatively high concentration in the base Portland cement material as well as the PFA and GGBS replacements. Hg also exceeded the EQS initially but thereafter was mostly less than the limit of detection (0.01 µg/l). The EQS for Hg (0.07 µg/l) is so low, it would require specialist analytical methods to accurately measure trends in the leaching rate. Lead would, in some cases, exceed the annual average EQS but

given the leaching appears to be largely ephemeral in comparison with the short-term, maximum admissible concentration (MAC) would be more appropriate and the critical EQS value of 14 µg/l was never exceeded at any point. The same could be said about Cr, with the annual average of 0.6 µg/l being exceeded for all treatments, but not the MAC (32 µg/l). There are no UK EQS for Mo, Se, or Ba. Although comparison with these EQS is in some ways indicative of potential impacts, the actual exposure scenarios for organisms in the vicinity to concretes in the environment may differ significantly.

Based on likely exposure scenarios, it may be expected that the metal leached would at worst only cause impacts for a limited time as leaching occurs, and only at the very surface of the substrate or in an enclosed environment such as a disused dock with no tidal exchange. In reality, actual impacts will also depend on the speciation of the metal, which controls its bioaccessibility (Van veen et al. 2001). The fact that concentrations of metals leached from the PFA and GGBS amended concretes were of no higher magnitude than that of the Portland cement-based matrix suggests the benefits of using these replacement materials outweigh the risks. However, the findings of this study need to be tempered by the fact that the metal content of PFA and GGBS can vary significantly between sources of waste material. As an example, Hg can occur in PFA at over 20 times higher concentrations, Cd 5 times higher, Zn and Cr 3 times higher concentrations and Cu, Ni and As typically 2 times higher. For GGBS, Cd can be up to 40 times higher in other similar materials, Cu 30 times, Pb 20 times, Cr 5 times and Zn 2 times. These variations suggest that careful analysis of the replacement materials might be required prior to use within sensitive environments.

4.2 Effects on colonising biofilm assemblages

There was a significant main effect of concrete type on biofilm % cover, but post hoc SNK tests failed to detect differences between paired comparisons. SNK tests are not as sensitive to differences as F tests (ANOVA); in this instance, effect sizes were insufficiently large to assign any effect of concrete type to any differences in biofilm % cover. Additionally, there was no significant effect of concrete type on biofilm richness, suggesting that the cement replacements used have little or no effect on the development of colonising biofilms, at least not in the proportions used. Whilst some studies have found that surface chemistry affects colonising biofilm assemblages (Ista et al. 2004), others have suggested that it may be more important for bacteria than for microalgae (Cooksey and Wigglesworth-Cooksey, 1995).

Given the expertise available, we focussed only on diatoms. We acknowledge that this is a limitation of the present work and suggest that future studies should focus on all biofilm assemblages, particularly if there are differential responses to surface chemistry. Cloning and sequencing of 16S rRNA genes would also identify any effects on bacterial communities present in the biofilm (Lee et al. 2008). This could prove an important factor later in succession, as biofilm dynamics are thought to play a major role in accelerating the settlement of macro-algae (Park et al. 2011) and succession by invertebrates on artificial surfaces (Siboni et al. 2007), with implications for antifouling technologies and aquaculture (Qian et al. 2007). Research has suggested that differences in the dynamics of microbial biofilms can alter (enhance or inhibit) precipitation of calcium carbonate onto artificial structures, having implications for engineering applications such as bio-grouting and self-healing concrete (Darquennes et al. 2016; Decho, 2010). As this study has focused on the early successional phases of biofilms over a 7-wk period, we are therefore unable to shed further light on the role of biofilms in promoting later successional phases and long-term development of macrofouling communities, although this may well be an important process in the colonisation of artificial structures post-construction.

It is important to note that in this study, the largest total cement replacement was 48%, whereas cement replacements of up to 80% GGBS and 50% PFA are routinely used in the marine environment (Chalee et al. 2010; Thomas and Matthews, 2004). They therefore have the potential to have a much greater effect on surface chemistry and therefore biofouling assemblages.

4.3 Effects on colonising macro-fouling assemblages

The control treatment exhibited highest native species richness which generally decreased significantly with the addition of GGBS. The addition of PFA alone had no significant effect on native species richness compared to the Portland cement control. Conversely, the replacement of cement with GGBS (in both GGBS only and Mixed treatments) significantly lowered native species richness compared to the control, suggesting that GGBS may have a greater negative effect on macro-fouling species than PFA. Leaching tests, however, showed slight, but statistically different leaching characteristics, with the concrete containing GGBS leaching less metal overall (Fig. 1), but individual metal concentrations did vary. GGBS contained higher concentrations of Zn and Ba, but lower in all of the other metals

detected compared with PFA or Portland cement. The higher Zn content of GGBS could, for example, have an impact owing to its biocidal properties, exploited in anti-fouling paints using active ingredients such as zinc pyrithione (Cima & Ballarin, 2015). Interestingly, both PFA and GGBS contained lower concentrations of Cu than the cement, which too, has biocidal properties and is widely used in anti-fouling paints. Whether it is these specific elements that are having an impact on the species richness or possibly more likely, colonisation is being controlled by surface interactions affecting the bioavailability and speciation of the leaching metals rather than impacts within the bulk solution would need further elucidation.

As concrete types with cement replaced by GGBS exhibited lower native species richness, it can be inferred that these communities have a lower stability and a lessened ability to recover from disturbance events (Oliver et al. 2015). Given the fact that the concrete types tested in this study had relatively low percentage replacements of cement, ecological effects may be even greater in marine concretes of higher cement replacement. Alternatively, differences could be down to effects other than this such as micro-scale differences in surface roughness caused by the cement replacements, although the lack of effect on biofilm cover does not lend itself to this conclusion.

Concrete type had a significant effect on native species composition. Macro-fouling assemblages associated with the control treatment exhibited the highest similarity compared to the Mixed treatment exhibiting the lowest similarity (Figure 5), suggesting that the assemblages that colonise Portland cement CMI are fairly homogenous and comprise a predictable suite of species. Conversely, assemblages that colonise CMI comprising a mixture of cement replacements are less predictable and are comprised of a greater range of species with varying tolerances to the chemicals associated with the cement replacements.

There were no significant differences in mean richness, mean proportion or composition of non-native species among concrete types. Many studies have stated that artificial structures facilitate the spread of marine invasive species (Airoldi et al. 2015; Mineur et al. 2012; Simkanin et al. 2012). Although this is usually attributed to low habitat heterogeneity, results here suggest that differences in relative abundance of non-native species may be due to the harsher chemical environment, where invasive and opportunistic species can thrive (Como

and Magni, 2009). The results suggest that although concrete CMI may facilitate threats to native biodiversity, there may be ways of limiting this by altering the materials used in marine concretes. Biological invasions by non-native species are acknowledged as one of the most important factors affecting the structure and functioning of marine ecosystems (Ojaveer and Kotta, 2015). They generally threaten native species and lower conservation value (Kernan, 2015). Whilst it is often thought that native species outperform non-natives in an ecosystem function role (Strayer, 2012), recent studies are finding that non-natives are in fact performing at similar (Zwersche et al. 2016) and sometimes higher levels than their native equivalents (Borsje et al. 2011). Despite this, it has been suggested that non-native species do not generally impair ecosystem function, and may actually expand it by adding new ecological traits, expanding existing ones and increasing redundancy of functional groups (Reise et al. 2006). Some research has even highlighted that as biological invasions are ultimately inevitable because of climate change, non-native species may become integral to future conservation plans, and may even become valued for the ecosystem services they provide, particularly as they tend to be more resilient and persistent than their indigenous counterparts (Hobbs et al. 2006; Schlaepfer et al. 2011).

4.4 Future research directions

This study represents one of the first studies to empirically combine chemical leaching data with biological data of micro- and macro-fouling species. It must be acknowledged that the results presented here reflect a very short-term study carried out over just 7-wk at a single location. Despite the limitations of the conclusions that can be drawn from a small-scale study such as this, we argue that the study system warrants further investigation to better understand the potential broader implications of cement replacement by waste aggregates. Future studies should consider all micro-organisms present in the biofilm and not just diatoms. Here, macro-fouling species were only assessed after 7 wk and a longer-term study would be beneficial to better understand colonisation patterns and the role of biofilms in facilitating macro-fouling on artificial structures. Furthermore, % cover of both macro- and micro-fouling assemblages (including bacteria) should be considered as much insight can be gained from assessing live cover in addition to species richness. Given that CMI can span the entire vertical gradient from subtidal to intertidal, it is very possible that the chemical leaching from the concrete may interact with air, and indeed there may be interactions with local weather conditions (temperature, precipitation); therefore, we advocate that future work

should conduct experiments in both the intertidal and subtidal environment and across the salinity gradient.

5. Conclusions

Native species richness and composition was affected by concrete type, but non-native species richness and composition was unaffected. This implies that the use of different concrete types does not influence the ability of non-native species to colonise the concrete surface, but does appear to impact native species. Sella and Perkol-Finkel (2015) highlighted the lower abundance of invasive species and higher abundance, richness and diversity on native species on EConcrete® compared to regular concrete. This branded version of environmentally friendly concrete has a lower pH (9–10.5) compared to a standard Portland cement (12.5–13.5). This research supports the conclusion that differences in species richness on different concrete types are potentially caused by differences in surface chemistry.

5.1 Potential applications of the results

The information presented in this study could be used to inform further research to enhance the ecological value of concrete marine infrastructure by enhancing ecosystem services, as well as by adding nature conservation value. Studies have shown that biodiversity associated with sea-defences has beneficial effects, such as attenuating waves, trapping sediments and even strengthening the structures (*sensu* 'bioprotection'; Gowell et al. 2015; Risinger, 2012; Coombes et al. 2017). This dynamic interaction between ecology, chemistry and engineering can be implemented to enhance the ecological potential of coastal defences. This research suggests that chemical composition should also be considered when designing artificial structures.

Concrete is the major construction material used in the creation structures like harbour walls, marinas and other semi-enclosed marine environments. In such places, a high level of human activity (Knights et al. 2011; Pearson et al. 2016) often means that water quality is compromised by high concentrations of nutrients leading to algal blooms (de Jonge et al. 2002). It may be possible to enhance ecosystem functions like filter-feeding by tailoring attachment substrate for desired species, and improve water quality through biofiltration

(Wilkinson et al. 1996). Other marine structures, such as artificial reefs, could benefit from manipulating the biodiversity present, whilst providing a more suitable material than for example, old tyres which have been used previously (Morely et al. 2008) to construct better artificial reefs, with a more natural benthic community, in turn encouraging a more natural structure of associated fish populations (Perkol-Finkel and Benayahu, 2007).

Extensive research has shown that physical features of artificial marine structures such as topographic complexity and water retaining features have a major role in enhancing their ecological attributes. However, results presented here highlight the fact that differences in concrete composition can have significant effects on the biodiversity of subtidal fouling organisms that colonise artificial surfaces. This information could be used in future to help design features that enhance biodiversity and the ecosystem services this provides at little or no extra cost.

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References

- Achternbosch, M., Kupsch, C., Nieke, E., Sardemann, G., 2011. Climate-friendly production of cement: a utopian vision?. *Gaia - Ecol. Perspect. Sci. Soc.* 20(1), 31-40.
- Aguilera, M.A., Broitman, B.R., Thiel, M., 2014. Spatial variability in community composition on a granite breakwater versus natural rocky shores: lack of microhabitats suppresses intertidal biodiversity. *Mar. Poll. Bull.* 87(1), 257-268.
- Airolidi, L., Turon, X., Perkol-Finkel, S., Rius, M., 2015. Corridors for aliens but not for natives: effects of marine urban sprawl at a regional scale. *Divers. Distrib.* 21(7), 755-768.
- Anderson, M.J., Underwood, A.J., 1994. Effects of substratum on the recruitment and development of an intertidal estuarine fouling assemblage. *J. Exp. Mar. Biol. Ecol.* 184(2), 217-236.
- Anderson M.J. 1996. A chemical cue induces settlement of Sydney rock oysters, *saccostrea commercialis*, in the laboratory and in the field. *Biolog. Bull.*, 190 (3), 350-358.
- Anderson, M.J., 2001. A new method for non-parametric multivariate analysis of variance *Austr. Ecol.* 26, 32-46.
- Ank, G., Porto, T.F., Pereira, R.C., da Gama, B.A.P., 2009. Effects of different biotic substrata on mussel attachment. *Biofouling*, 25(2), 173-180.
- Arenas, F., Bishop, J.D.D., Carlton, J.T., Dyrinda, P.J., Gonzalez, D.J., Jacobs, M.W., Lambert, C., Lambert, G., Nielsen, S.E., Pederson, J.A., Ward, S., Wood, C.A., 2006. Alien species and other notable records from a rapid assessment survey of marinas on the south coast of England. *J. Mar. Biol. Ass. UK* 86(6), 1329-1337.
- Bignozzi, M.C., 2011. Sustainable cements for green buildings construction. *Procedia Engineer.* 21, 915-921.
- Bishop, J.D., Roby, C., Yunnies, A.L., Wood, C.A., Lévêque, L., Turon, X., Viard, F., 2013. The Southern Hemisphere ascidian *Asterocarpa humilis* is unrecognised but widely established in NW France and Great Britain. *Biol. Invas.* 15(2), 253-260.
- Bishop, M.J., Mayer-Pinto, M., Airolidi, L., Firth, L.B., Morris, R.L., Loke, L.H., Hawkins, S.J., Naylor, L.A., Coleman, R.A., Chee, S.Y. and Dafforn, K.A., 2017. Effects of ocean sprawl on ecological connectivity: impacts and solutions. *J. Exp. Mar. Biol. Ecol.* 492, 7-30.
- Borsje, B.W., van Wesenbeeck, B.K., Dekker, F., Paalvast, P., Bouma, T.J., van Katwijk, M.M., de Vries, M.B., 2011. How ecological engineering can serve in coastal protection. *Ecol. Engineer.* 37, 113-122.
- Brigden, K., Santillo, D., 2002. Heavy metal and metalloid content of fly ash collected from the Sual, Mauban and Masinloc coal-fired power plants in the Philippines. Technical note (07/2002) for Greenpeace, Exeter, UK.

- British Standards Institute. 2011. BS EN 197-1: 2011. [Online]. Available from:
<http://shop.bsigroup.com/ProductDetail/?pid=000000000030331489>. [Accessed on:
 02/08/16].
- Brown, C.J., 2005. Epifaunal colonization of the Loch Linnhe artificial reef: Influence of
 substratum on epifaunal assemblage structure. *Biofouling* 21(2), 73-85.
- Bulleri, F., Airoidi, L., 2005. Artificial marine structures facilitate the spread of non-indigenous
 green alga, *Codium fragile* ssp. *tomentosoides*, in the north Adriatic Sea. *J. Appl. Ecol.*
 42(6), 1063-1072.
- Bulleri, F., Chapman, M.G., 2009. The introduction of coastal infrastructure as a driver of
 change in marine environments. *J. Appl. Ecol.* 47(1), 26-35.
- Burt, J., Bartholomew, A., Usseglio, P., Bauman, A., Sale, P.F., 2009. Are artificial reefs
 surrogates of natural habitats for corals and fish in Dubai, United Arab Emirates?. *Coral*
Reefs, 28(3), 663-675.
- Chalee, W., Ausapanit, P., Jaturapitakkul, C., 2010. Utilization of fly ash concrete in marine
 environment for long term design life analysis. *Materials & Design* 31(3), 1242-1249.
- Chapman, M.G., 2006. Intertidal seawalls as habitats for molluscs. *J. Mollusc. Stud.* 72(3),
 247-257.
- Chapman, M.G., Underwood, A.J., 2011. Evaluation of ecological engineering of "armoured"
 shorelines to improve their value as habitat. *J. Exp. Mar. Biol. Ecol.* 400(1), 302-313.
- Cima, F., Ballarin, L., 2015. Immunotoxicity in ascidians: antifouling compounds alternative
 to organotoxins-IV. The case of zinc pyrithione. *Comp. Biochem. Physiol. C.* 169, 16-24.
- Clarke, K., 1993 Non-parametric multivariate analyses of changes in community structure
Austr. J. Ecol. 18, 117-43.
- Clarke, K.R., Warwick, R.M. 1994. PRIMER: Plymouth Routines in Multivariate Ecological
 Research, a suite of computer programmes (Plymouth: Plymouth Marine Laboratory).
- Como, S., Magni, P., 2009. Temporal changes of a macrobenthic assemblage in harsh
 lagoon sediments. *Estuar. Coast. Shelf. Sci.* 83(4), 638-646.
- Connell, S. D., 2000. Floating pontoons create novel habitats for subtidal epibiota. *J. Exp.*
Mar. Biol. Ecol. 247(2), 183-194.
- Cooksey, K. E., Wigglesworth-Cooksey, B., 1995. Adhesion of bacteria and diatoms to
 surfaces in the sea - A review. *Aquatic Micro. Ecol.* 9(1), 87-96.
- Coombes, M.A., La Marca, E.C., Naylor, L.A., Thompson, R.C., 2015. Getting into the
 groove: Opportunities to enhance the ecological value of hard coastal infrastructure using
 fine-scale surface textures. *Ecol. Engineer.* 77, 314-323.

- Coombes, M.A., Viles, H.A., Naylor, L.A. and La Marca, E.C., 2017. Cool barnacles: Do common biogenic structures enhance or retard rates of deterioration of intertidal rocks and concrete?. Sci. Tot. Environ. 580, 1034-1045.
- Dafforn, K.A., Glasby, T.M., Airoidi, L., Rivero, N.K., Mayer-Pinto, M., Johnston, E.L., 2015. Marine urbanization: an ecological framework for designing multifunctional artificial structures. Front. Ecol. Environ. 13(2), 82-90.
- Darquennes, A., Olivier, K., Benboudjema, F., Gange, R., 2016. Self-healing at early-age, a way to improve the chloride resistance of blast-furnace slag cementitious materials. Construct. Building Materials, 113, 1017-1028.
- Decho, A.W., 2010. Overview of biopolymer-induced mineralization: what goes on in biofilms?. Ecol. Engineer. 36(2), 137-144.
- de Jonge, V.N., Elliot, M., Orive, E., 2002. Caused, historical development, effects and future challenges of a common environmental problem: eutrophication. Hydrobiologia, 475(1), 1-19.
- Dennis, H., Moore, P.J., Banner, A. and Evans, A.J., 2017. Reefcrete: reducing the environmental footprint of concretes for engineered marine structures. Ecol. Engineer. In Press. **This issue**, <https://doi.org/10.1016/j.ecoleng.2017.05.031>
- EU (2013) Council of the European Parliament, 2011/0429 (COD), LEX 1369. Directive Of The European Parliament and of the Council Amending Directives 2000/60/EC And 2008/105/EC As Regards Priority Substances In The Field Of Water Policy.
- Evans, A.J., Garrod, B., Firth, L.B., Hawkins, S.J., Morris-Webb, E.S., Goudge, H. and Moore, P.J., 2017. Stakeholder priorities for multi-functional coastal defence developments and steps to effective implementation. Mar. Pol. 75, 143-155.
- Firth, L.B., Knights, A.M. and Bell, S.S., 2011. Air temperature and winter mortality: implications for the persistence of the invasive mussel, *Perna viridis* in the intertidal zone of the south-eastern United States. J. Exp. Mar. Biol. Ecol. 400, 250-256.
- Firth, L.B., Thompson, R.C., White, F.J., Schofield, M., Skov, M.W., Hoggart, S.P.G., Jackson, J., Knights, A.M., 2013. The importance of water retaining features for biodiversity on artificial intertidal coastal defence structures. Divers. Distrib. 19(10), 1275-1283.
- Firth, L.B., Mieszkowska, N., Grant, L.M., Bush, L.E., Davies, A.J., Frost, M.T., Moschella, P.S., Burrows, M.T., Cunningham, P.N., Dye, S.R. and Hawkins, S.J., 2015. Historical comparisons reveal multiple drivers of decadal change of an ecosystem engineer at the range edge. Ecol. Evol. 5(15), 3210-3222.
- Firth, L.B., Knights, A.M., Thompson, R.C., Mieszkowska, N., Bridger, D., Evans, A.J., Moore, P.J., O'Connor, N.E., Sheehan, E.V., Hawkins, S.J. 2016a. Ocean sprawl: challenges and opportunities for biodiversity management in a changing world. Oceanogr. Mar. Biol. Ann. Rev. 54, 193-269.

- Firth, L.B., Browne, K., Knights, A.M., Hawkins, S.J., Nash, R., 2016b. Eco-engineered rock pools: a concrete solution to biodiversity loss and urban sprawl in the marine environment. *Environ. Res. Lett.* 11, 094015.
- Gowell, M., Coombes, M.A., Viles, H.A., 2015. Rock-protecting seaweed? Experimental evidence of bioprotection in the intertidal zone. *Earth Surf. Proc. Landform.* 40(10): 1364-1370.
- Graham, R.K., Huang, B., Shu, X., Burdette, E.G., 2013. Laboratory evaluation of tensile strength and energy absorbing properties of cement mortar reinforced with micro-and meso-sized carbon fibers. *Construct. Building Materials*, 44, 751-756.
- Griffin, J.N., Laure, M.L.N., Crowe, T.P., Burrows, M.T., Hawkins, S.J., Thompson, R.C., Jenkins, S.R., 2010. Consumer effects on ecosystem functioning in rock pools: roles of species richness and composition. *Mar. Ecol. Progr. Ser.* 420, 45-56.
- Harlin, M.M., Lindbergh, J.M., 1977. Selection of substrata by seaweeds: optimal surface relief. *Mar. Biol.* 40(1), 33-40.
- Hobbs, R.J., Arico, S., Aronson, J., Baron, J.S., Bridgewater, P., Cramer, V.A., Epstein, P.R., Ewel, J.J., Klink, C.A., Lugo, A.E. and Norton, D., 2006. Novel ecosystems: theoretical and management aspects of the new ecological world order. *Glob. Ecol. Biogeog.* 15(1), 1-7.
- Ilyushechkin, A.Y., Roberts, D.G., French, D., Harris, D.J., 2012. IGCC Solids Disposal and Utilisation, Final Report for ANLEC Project 5-0710-0065. CSIRO, Australia.
- Ista, L.K., Callow, M.E., Finlay, J.A., Coleman, S.E., Nolasco, A.C., Simons, R.H., Callow, J.A., Lopez, G.P., 2004. Effect of substratum surface chemistry and surface energy on attachment of marine bacteria and algal spores. *Appl. Env. Micro.* 70(7), 4151-4157.
- Izquierdo, M., Querol, X., Davidovits, J., Antenucci, D., Nugteren, H., Fernandez-Pereira, C., 2009. Coal fly ash-slag based geopolymers: Microstructure and metal leaching. *J. Hazard. Material.* 166, 561-566.
- Jang, J.G., Ahn, Y.B., Souri, H., Lee, H.K., 2015. A novel eco-friendly porous concrete fabricated with coal ash and geopolymeric binder: Heavy metal leaching characteristics and compressive strength. *Construct. Build. Material.* 79. 173-181.
- Kampa, E., Laaser, C., 2009. Heavily modified water bodies: Information exchange on designation, assessment of ecological potential, objective setting and measures, Brussels, Belgium: Common Implementation Strategy Workshop.
- Kernan, M., 2015. Climate change and the impact of invasive species on aquatic ecosystems. *Aquat. Ecosys. Health Manage.* 18(3), 321-333.
- Knights, A.M., Firth, L.B., Thompson, R.C., Yunnice, A.L., Hiscock, K., Hawkins, S.J., 2016. Plymouth—A World Harbour through the ages. *Reg. Stud. Mar. Sci.* 8. 297-307.
- Knights, A.M. Koss, R.S., Papadopoulou, K.N., Cooper, L.H., Robinson, L.A. 2011. Sustainable use of European regional seas and the role of the Marine Strategy Framework Directive. Liverpool: University of Liverpool.

- Langston, W.J., Chesman, B.S., Burt, G.R., Hawkins, S.J., Readman, J. Worsfold, P., 2003.
 Characterisation of the South West European Marine Sites. Plymouth Sound and Estuaries
 cSAC, SPA. Occ. Pub. Mar. Biol. Assoc. UK (9) 202p.
- Lee, J.W., Nam, J.H., Kim, Y.H., Lee, K.H., Lee, D.H., 2008. Bacterial communities in the
 initial stage of marine biofilm formation on artificial surfaces. J. Microbiol. 46(2), 174-182.
- Mineur, F., Cook, E.J., Minchin, D., Bohn, K., MacLeod, A., Maggs, C.A., 2012. Changing
 coasts: marine aliens and artificial structures. Oceanogr. Mar. Biol. Ann. Rev. 50, 189-233.
- Morely, D.M., Sherman, R.L., Jordan, L.K.B., Banks, K.W., Quinn, T.P., Spieler, R.E., 2008.
 Environmental enhancement gone awry: Characterization of an artificial reef constructed
 from waste vehicle tyres. Envir. Prob. Coast. Reg. VII. 99, 73-87.
- Moreno, N., Querol, X., Andrés, J.M., Stanton, K., Towler, M., Nugteren, H., Janssen-
 Jurkovicová, M., Jones, R., 2005. Physico-chemical characteristics of European pulverized
 coal combustion fly ashes. Fuel 84(11), 1351-1363.
- Morris, R.L., Deavin, G., Hemelryk Donald, S. and Coleman, R.A., 2016. Eco-engineering in
 urbanised coastal systems: consideration of social values. Ecol. Manage. Restor. 17(1), 33-
 39.
- Moschella, P.S., Abbiati, M., Aberg, P., Airoidi, L., Anderson, F., Bacchiocchi, F., Bulleri, F.,
 Dinesen, G.E., Frost, M., Gacia, E., Granhag, L., Jonsson, P.R., Satta, M.P., Sundelorf, A.,
 Thompson, R.C., Hawkins, S.J., 2005. Low-crested coastal defence structures as artificial
 habitats for marine life: Using ecological criteria in design. Coast. Engineer. 52(10-11),
 1053-1071.
- Müllauer, W., Beddoe, R.E., Heinz, D., 2015. Leaching behaviour of major and trace
 elements from concrete: effect of fly ash and GGBS. Cement and Concrete Composites, 58,
 129-139.
- Nandakumar, K., Matsunaga, H., Takagi, M., 2003. Microfouling studies on experiemetal
 test blocks of steel-making slag and concrete exposed to seawater off Chiba, Japan.
 Biofouling 19(4), 257-267.
- Neo, M.L., Todd, P.A., Teo, S.L., Chou, L.M., 2009. Can artificial substrates enriched with
 crustose coralline algae enhance larval settlement and recruitment in the fluted giant clam
 (*Tridacna squamosa*)?. Hydrobiologia 625, 83-90.
- Nicholls, R.J., Kebede, A.S., 2012. Indirect impacts of coastal climate change and sea-level
 rise: the UK example. Climate Policy 12(SI), S28-S52.
- Ojaveer, H., Kotta, J., 2015. Ecosystem impacts of the widespread non-indigenous species
 in the Baltic Sea: literature survey evidences major limitations in knowledge. Hydrobiologia
 750(1), 171-185
- Oliver, T.H., Heard, M.S., Isaac, N.J.B., Roy, D.B., Procter, D., Eigenbrod, F., Freckleton, R.,
 Hector, A., Orme, C.D.L., Petchey, O. L., Proenca, V., Raffaelli, D., Suttle, K. B., Mace, G.

- M., Martin-Lopez, B., Woodcock, B.A., Bullock, J.M., 2015. Biodiversity and resilience of
 ecosystem functions. *Trend. Ecol. Evol.* 30(11), 673-684.
- Oksanen, J., Blanchet, F.G., Kindt, R., Legendre, P., Minchin, P.R., O'Hara, R.B., Simpson,
 G.L., Solymos, P., Stevens, M.H.H., Wagner, H., Oksanen, M.J., 2013. Package 'vegan'.
 Community ecology package, version, 2(9).
- Park, S.R., Kang, Y.H. & Choi, C.G., 2011. Biofilm: A crucial factor affecting the settlement
 of seaweed on intertidal rocky surfaces. *Est. Coast. Shelf Sci.*, 91(1), pp. 163-167.
- Pavia, S., Condren, E. 2008. Study of the Durability of OPC versus GGBS Concrete on
 Exposure to Silage Effluent. *J. Mat. Civ. Eng.* 20, 313-320.
- Pearson, S., Windupranata, W., Pranowo, S.W., Putri, A., Ma, Y., Vila-Concejo, A.,
 Fernández, E., Méndez, G., Banks, J., Knights, A.M. and Firth, L.B., Breen, B. B., Jarvis, R.,
 Aguirre, J. D., Chen, S., Smith, A. N. H., Steinberg, P., Chatzinikolaou, E., Arvanitidis C.,
 2016. Conflicts in some of the World harbours: what needs to happen next?. *Mar. Stud.* 15,
 p.10.
- Perkol-Finkel, S., Benayahu, Y., 2007. Differential recruitment of benthic communities on
 neighboring artificial and natural reefs. *J. Exp. Mar. Biol. Ecol.* 340(1), 25-39.
- Perkol-Finkel, S., Sella, I., 2015. Blue is the new green - Ecological enhancement of
 concrete based coastal and marine infrastructure. *Ecol. Engineer.* 84, 260-272.
- Pomerat, C.M., Weiss, C.M., 1946. The influence of texture and composition of surface on
 the attachment of sedentary marine organisms. *Biol. Bull.* 91(1), 57-65.
- Qian, P.Y., Lau, S.C.K., Dahms, H.U., Dobretsov, S., Harder, T., 2007. Marine biofilms as
 mediators of colonisation by marine macroorganisms: implications for antifouling and
 aquaculture. *Mar. Biotech.* 9(4), 399-410.
- Reise, K., Olenin, S., Thielges, D.W., 2006. Are aliens threatening European aquatic coastal
 ecosystems?. *Helgoland Mar. Res.*, 60(2), 77-83.
- Risinger, J.D., 2012. Biologically dominated engineered coastal break-waters. PhD Thesis,
 p. Louisiana State University and Agricultural and Mechanical College.
- Salta, M., Wharton, J.A., Blache, Y., Stokes, K.R., Briand, J.F., 2013. Marine biofilms on
 artificial surfaces: structure and dynamics. *Env. Microbiol.* 15(11), 2879-2893.
- Sanz-Lazaro, C., Fodelianakis, S., Guerrero-Meseguer, L., Marin, A., Karakassis, I., 2015.
 Effects of organic pollution on biological communities of marine biofilm on hard substrata.
Env. Poll. 201, 17-25.
- Satheesh, S., Wesley, S.G., 2010. Influence of substratum colour on the recruitment of
 macrofouling communities. *J. Mar. Biol. Ass. UK.* 90(5), 941-946.
- Schlaepfer, M.A., Sax, D.F., Olden, J.D., 2011. The potential conservation value of non-
 native species. *Conserv. Biol.* 25(3), 428-437.

- Scyphers, S.B., Powers, S.P., Akins, J.L., Drymon, J.M., Martin, C.W., Schobernd, Z.H.,
 Schofield, P.J., Shipp, R.L. and Switzer, T.S., 2015. The role of citizens in detecting and
 responding to a rapid marine invasion. *Conserv. Lett.* 8(4), 242-250.
- Seaman, W., 2007. Artificial habitats and the restoration of degraded marine ecosystems
 and fisheries. *Hydrobiologia* 580(1), 143-155.
- Sella, I., Perkol-Finkel, S., 2015. Harnessing urban coastal infrastructure for ecological
 enhancement. *Proc. Inst.Civil Engineer.* 168(3), 102-110.
- Shi, H.S., Kan, L.L., 2009. Leaching behavior of heavy metals from municipal solid wastes
 incineration (MSWI) fly ash used in concrete. *J. Hazard. Material.* 164(2), 750-754.
- Siboni, N., Lidor, M., Kramarsky-Winter, E., Kushmaro, A., 2007. Conditioning film and initial
 biofilm formation on ceramic tiles in the marine environment. *Fems Micro. Lett.* 274, 24-29.
- Simkanin, C., Davidson, I.C., Dower, J.F., Jamieson, G., Therriault, T.W., 2012.
 Anthropogenic structures and the infiltration of natural benthos by invasive ascidians. *Mar.*
Ecol. 33(4), 499-511.
- Small, C., Nicholls, R.J., 2003. A global analysis of human settlement in coastal zones. *J.*
Coast. Res. 19, 584-599.
- Snelson, D.G., Kinuthia, J.M., 2010. Resistance of mortar containing unprocessed
 pulverised fuel ash (PFA) to sulphate attack. *Cement and Concrete Composites* 32(7), 523-
 531.
- Strayer, D.L., 2012. Eight questions about invasions and ecosystem functioning. *Ecol. Lett.*
 15(10), 1199-1210.
- Sweat, H. L., Johnson, K. B., 2013. The effects of fine-scale substratum roughness on
 diatom community structure in estuarine biofilms. *Biofouling* 29(8), 879-890.
- Thomas, M.D.A., Matthews, J.D., 2004. Performance of PFA concrete in a marine
 environment - 10-year results. *Cement & Concrete Composites* 26(1), 5-20.
- Van Jaarsveld, J.G.S., Van Deventer, J.S.J., Schwartzman, A., 1999. The potential use of
 geopolymeric materials to immobilise toxic metals: Part II. Material and leaching
 characteristics. *Minerals Engineer.* 12(1), 75-91.
- Van Veen E., Gardner M.J., Comber S.D.W., 2001. Temporal variation of copper and zinc
 complexation capacity in the Humber Estuary. *J. Env. Monitor.* 4, 116-120.
- WFD (2015) The Water Framework Directive (Standards and Classification), Directions
 (England and Wales) 2015.
- Wilkinson, S.B., Zheng, W., Allen, J.R., Fielding, N.F., Wanstall, V.C., Russel, G., Hawkins,
 S.J., 1996. Water quality improvements in Liverpool docks: The role of filter feeders in algal
 and nutrient dynamics. *Mar. Ecol.* 17(1-3), 197-211.

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foundation for ecological enhancement. Ecological Engineering,
<https://doi.org/10.1016/j.ecoleng.2017.06.062>

- 1031 Yu, Q., Nagataki, S., Lin, J., Saeki, T., Hisada, M., 2005. The leachability of heavy metals in
1032 hardened fly ash cement and cement-solidified fly ash. Cement and Concrete Res. 35(6),
1033 1056-1063.
- 1034 Zemajtis, J.Z., 2016. Role of Concrete Curing. [Online]. Available from:
1035 <http://www.cement.org/for-concrete-books-learning/concrete-technology/concrete->
1036 [construction/curing-in-construction.](http://www.cement.org/for-concrete-books-learning/concrete-technology/concrete-) [Accessed on: 02/08/16].
- 1037
1038 Zwerschke, N., Emmerson, M.C., Roberts, D., O'Connor, N.E., 2016. Benthic assemblages
1039 associated with native and non-native oysters are similar. Mar. Poll. Bull. 111(1), 305-310.
1040
1041
1042