

Chemical contamination of a coral reef by the grounding of a cruise ship in Bermuda

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Abstract

Bulk metal analyses of surficial sediments collected around the Norwegian Crown cruise ship grounding site in Bermuda indicated significant but localized contamination of reef sediments by copper and zinc, caused by the stripping of the tri-butyltin (TBT)-free anti-fouling (AF) paint (Intersmooth 460) from the underside of the hull. Highest copper and zinc values were found in heavily compacted and red-pigmented sediments inside the impact scar and were comparable to levels found close to slip ways of local boat yards where AF paints from hull stripping and cleaning processes are washed into the sea. The re-distribution of AF contaminated sediments by storms and deposition on nearby reefs constitutes a significant ecological risk that could delay recovery processes and reduce the effectiveness of remediation efforts. Whilst the ecotoxicological effects of AF paint particles interspersed with sediment is unknown, and in need of further study, it is argued that the significance of AF paint contamination of grounding sites has been overlooked.

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1. Introduction

Ship groundings on coral reefs often result in severe localized biological and physical damage, including the dislodgement of corals, pulverization of coral skeletons, displacement of sediment deposits, and loss of 3-dimensional complexity (Precht, 1998; Jaap, 2000; Precht et al., 2001; Precht and Robbart, 2006; Jaap et al., 2006). Between 500 and 600 vessel groundings are reported in the Florida Keys National Marine Sanctuary (FKNMS) annually and approximately 60–90 of the groundings have involved injuries to coral reef habitat (Andrews et al., 2005). Increasingly more of these ship grounding incidents are involving insurance claims to pay for triage, assessment and quantification of the damage, restoration and subsequent monitoring, compensatory restoration (compensating the public for the interim loss of the resource from the time the injury occurred until restoration is complete),

as well as punitive action. Scaling for compensation and restoration is based on assessing the extent of the injury and determining the time necessary for recovery to the pre-incident state (Andrews et al., 2005).

Most attention has been focused on the biological and the physical environment following a major ship grounding and comparatively little attention has been paid to the chemical environment. In the absence of loss of cargo or breaching of the ship's hull, the abrading, or excoriation, of the antifouling (AF) paint is perhaps the most likely form of contamination as the ship's hull comes into contact with the hard reef or coarse coral rock, sand and rubble in inter-reefal areas (for example see Figure 1.1 in Precht and Robbart, 2006, and Figure 16.1C in Jaap et al., 2006). These AF paints pose a significant ecological risk as they contain biocides specifically designed and chosen to prevent settlement and growth of algae and invertebrates.

In the summer of 2006 a cruise ship struck a coral reef in Bermuda. The AF paint used on the ship was Intersmooth 460 (International Marine Coatings) a Tributyltin (TBT)-free self polishing copolymer with copper oxide and zinc pyrithione as primary and secondary biocides. Less than

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48 h after the ship was refloated and removed from the reef, the grounding site was examined to assess the extent of damage and investigate the possibility that the sediments had been contaminated by AF paint abraded from the ship's hull.

2. Materials and methods

On Wednesday 7th June 2006, The Norwegian Cruise Line (NCL) cruise ship the *Norwegian Crown* (Length: 188 m, Gross Registered Tonnage: 34,242) grounded on sandy sediment at the edge of a navigation channel in Bermuda, eventually coming to rest tilted to starboard, on a small patch reef (Fig. 1, Bow of the Ship = 32°18'55.66"N, 64°49'35.35"W). The grounding occurred as the ship was commencing a turn from the southern shipping channel into Dundonald channel at the entrance to the Great Sound (Fig. 2). At the time of the incident (08:30 h) the ship was under compulsory pilotage, and was traveling on a bearing of 187° at a speed of 10.8 knots. As a result of the collision, and further exaggerated by efforts to lighten the ship during the refloat, the bulbous bow of the ship was lifted clear of the water (Fig. 1B). The incident occurred on an ebb-tide and attempts to refloat the ship in the morning by locally flagged tugs were unsuccessful (Fig. 1A). Substantial turbidity plumes stretching several kilometers were generated by these activities (Fig. 1A and

B). The cruise ship was eventually pulled backwards off the reef by tugs at 17:00 h on the early evening high tide.

The result of the grounding was an impact scar in the form of a ~120 m long trench (furrow) in the carbonate sediments. Either side of the impact scar, berms of displaced sand and coral rubble were formed. Several deep craters were also caused by the ship's propellers close to the edge of the shipping channel. The ship eventually came to rest on a small patch reef at the head of the impact furrow, causing the reef matrix to shatter, generating large amounts of coral rubble, and causing extensive structural damage including splitting the reef in several large (>1 m wide) fracture zones. Flakes of large (>1 cm) red AF paint were observed adhered onto broken coral heads on the forward port side of the impact furrow. Approximately 20–50 m from where the bow came to rest patches of sediments on the western sides of the impact furrow were heavily compacted, i.e. firm to touch, impregnated with shells and coral rubble and pigmented reddish/pink with AF paint particles (Fig. 1C).

Duplicate samples of surficial (upper 1–2 cm) sediments were taken for metal analyses within a 1–2 m radius of the centerline of the impact furrow at 5, 10, 20, 30, 40, 50 and 80 m along the main axis of the scar. At each of the 5, 10, 20, 40 and 80 m sampling points additional transect tapes were laid down at right angles to the centerline, and where possible single sediment samples were taken for metal anal-



Fig. 1. (A) Initial, unsuccessful, attempts by three locally flagged tugs to pull the 188 m *Norwegian Crown* cruise ship off a patch reef in Bermuda. Note the starboard list. (B) Emersion of the ship's bulbous during the refloating attempts. Note the impact scarring and excoriation of the antifouling paint from the vessel's hull. (C) Interspersion of antifouling paint flakes with sediment. Images (A) and (B) courtesy of David Skinner.

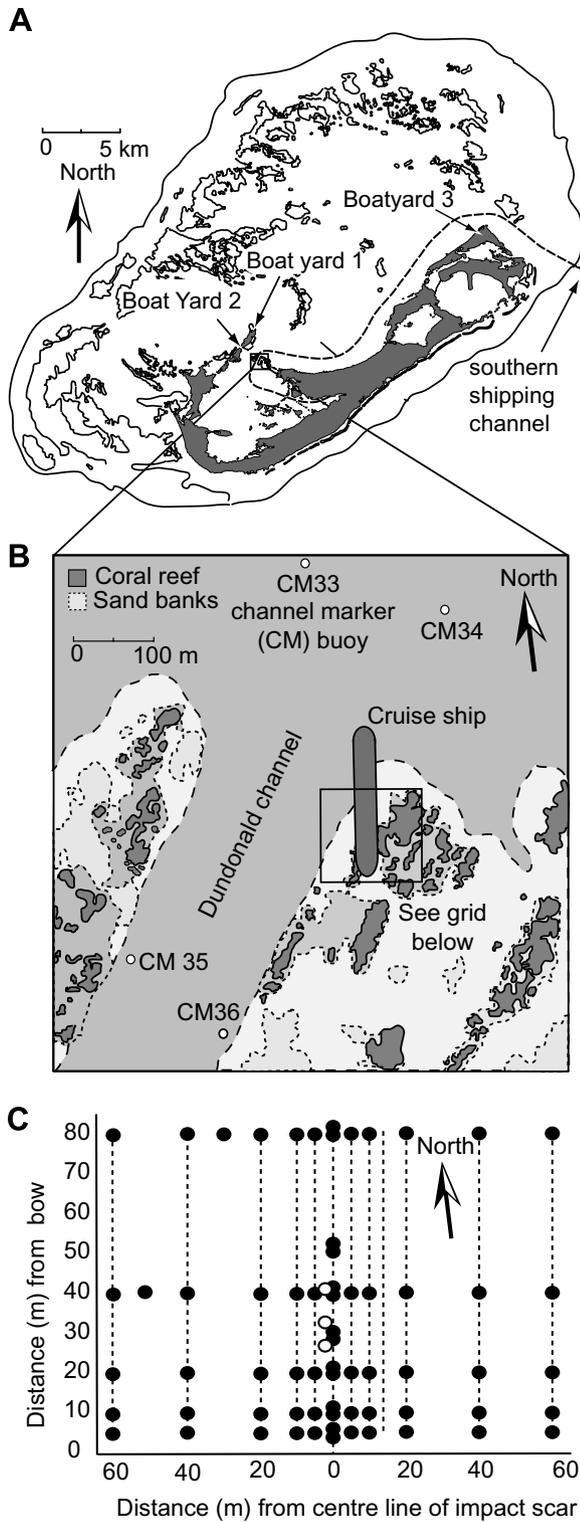


Fig. 2. (A)–(C) Location maps showing the cruise ship grounding site. (C) shows the sediment sampling points (black circles) located in, or east or west, of the impact furrow. White circles represent additional samples taken 28, 34 and 41 m back from where the bow came to rest on the western side of the impact furrow.

yses at 5, 10, 20, 40 and 60 m east and west from the centre of the furrow (see Fig. 2B). Additional chemical analyses were made of the compacted and pigmented sediments 28, 34, 41 m from where it was estimated the bow came to rest

and 2 m west of the centreline of the impact furrow. Surficial sediment samples were also taken of sub tidal sediments at 3–4 m within a 20 m radius of three boat yards in Bermuda (Fig. 2) where power washing of boats is known to occur. All sediments samples were collected by SCUBA divers and samples were placed in pre-cleaned 250 ml HDPE bottles. Bottles were soaked overnight in 10% HCl and rinsed three times with Milli-Q water before use. SCUBA divers used surgical gloves when collecting samples to prevent contamination. All samples were placed in coolers containing ice in the field, and in the laboratory were frozen prior to analysis which was conducted within 10 days of collection. Samples were analysed using EPA 3050 (Preparation method) and EPA 6020 (Analytical Method) with Inductively coupled plasma mass spectrometry (ICP/MS).

3. Results

Of the metals tested copper and zinc levels were clearly elevated at multiple locations within and outside the impact scar (Fig. 3). Levels tended to be highest in the impact furrow, and decreased (1) with increasing distance at right angles away from the centerline of the furrow, and (2) down the length of the impact furrow (Fig. 3). In general metal levels also tended to be higher on the eastern side of the impact furrow (i.e. between the ship and the patch reef) than on the western side. The furthest distance contaminated sediments were detected from the centre line of the impact furrow (i.e. laterally) was 20 m, where elevated copper concentrations were detected in the forward part of the furrow on the eastern side (Fig. 3). The highest copper and zinc values (4270 and 2710 mg/kg dry weight respectively) were recorded on the western side of the impact furrow 28 m from the where the bow came to rest (Fig. 3). This sediment was intentionally sampled as it appeared obviously pigmented with AF paint and the metal values were anticipated to be high. Of the sediment samples collected in which there was no visible pigmentation by AF paint (i.e. samples were collected because they were located under the sampling grid), the highest values were 754 and 390 mg/kg dry weight for copper and zinc respectively (Fig. 3). Samples taken 40 m and 60 m east and west of the centre line of the impact scar were below the detection limit (2 mg/kg dry weight for copper and 10 mg/kg dry weight for Zn).

All surficial sediment samples collected close to boatyards contained elevated metal levels, notably of copper, zinc and lead (Table 1). These values were 1000×, 100× and 75×, respectively higher than values found in uncontaminated calcium carbonate sediments, represented by those samples collected 60 m to the west of the centreline of the grounding site where levels were at or near the detection limits of the analytical techniques.

From the metal data, hierarchical clustering analysis was used to produce a dendrogram (tree diagram) in which a series of nested groupings of sites is constructed, with similarly contaminated samples clustering close together and dissim-

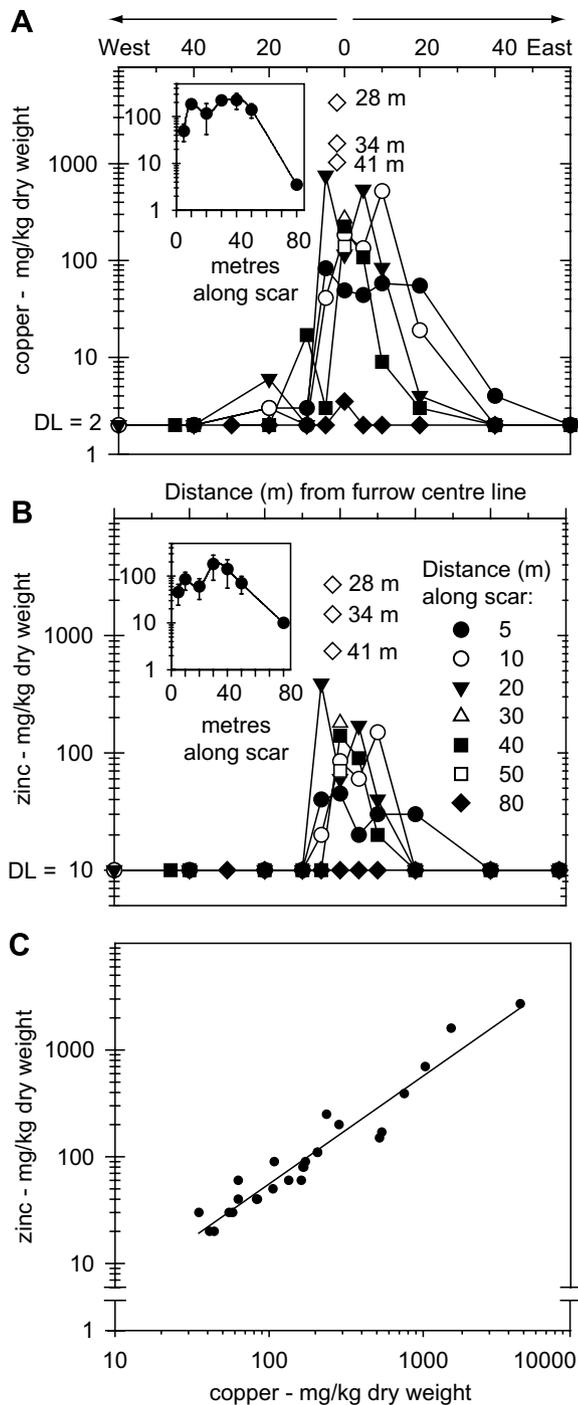


Fig. 3. (A) Copper and (B) zinc concentration (mg/kg dry weight) in sediments collected from the *Norwegian Crown* grounding site impact scar and surrounding areas. Duplicate samples were taken on the centreline of the impact scar at 5, 10, 20, 40, and 80 m from where the bow came to rest (data shown as means of 2 samples). Single samples were then taken at 5, 10, 20, and where possible, 40 and 60 m east or west of the sampling points in the impact scar. Additional samples (white diamonds) were taken at 28, 34 and 41 m where sediment was clearly contaminated with antifouling paints (i.e. the sediments were pigmented red or pink). Note the log scale on all y-axes. Inset figures represent the mean (\pm SD) of duplicate samples taken on the centreline of the impact scar. (C) Correlation curve between copper and zinc concentration (mg/kg dry weight) in sediments collected from the *Norwegian Crown* grounding site impact scar where values for both copper and zinc exceed the analytical detection limits ($r = 0.87$). Note the log scale on both axes.

ilar samples spaced farther apart (Fig. 4). Several clusters can be identified, including samples taken of the pigmented (clearly contaminated) sediments (cluster 1), sediment samples collected close (i.e. less than 20 m) to the centreline of the impact furrow and close to where the bow came to rest (cluster 2), and the remaining samples (cluster 3).

Principle component (PC) analysis (PCA) was performed on a table of sample sites and metals levels. Fig. 5 shows the relationship between the first 2 Eigen vectors. The PCA plot indicates a progression from heavily contaminated samples on the left hand-side, through moderately contaminated sediments in the middle, to uncontaminated sediments on the right-hand-side. PCs are products of the eigenvalue and the corresponding eigenvector. The total variance that can be explained by a PC is reflected in the eigen value and in this instance, a significant 87.9% of the total variability is accounted for by PC1 with only a further 5.6% by PC2 (cumulative value = 93.5%). This indicates that the 2-dimensional ordination is likely to be highly representative of the true order of the matrix in multidimensional space. Eigenvectors are composed of coefficients that reflect the contribution of their respective variables to the variance of that PC. The first PC had highest coefficients on copper and then zinc (data not shown).

4. Discussion

In addition to the obvious structural and biological damage caused to the reef by the grounding of the *Norwegian Crown*, bulk chemical analyses of the surficial sediments at the impact site present a clear and coherent picture of contamination by the copper and zinc-containing antifouling (AF) paint used on the cruise ship's hull.

Overall copper concentrations in the most contaminated samples (700–4270 mg/kg dry weight) were considerably higher than values reported by Haynes and Loong (2002) for two commercial harbours associated with intensive shipping and industrial activity in an equivalent marine environment i.e. tropical Cairns and Townsville, Australia, Great Barrier Reef region, where values of 28–140 mg/kg dry weight and 37–233 mg/kg dry weight were measured respectively. These areas are impacted from hull cleaning and stormwater runoff from large urban centres. The values for copper and zinc in the most contaminated grounding site samples were similar to values found in sub-tidal sediments beside slipways of three boat yards in Bermuda where it is known that boat hulls are cleaned and antifouling paint flakes can be washed directly into the sea. In Florida coastal waters paint chips and sanding dust must be collected for disposal at a permitted landfill and on-site solid waste disposal of paint chips and sanding dust on land or water is prohibited. Clearly similar rules and regulations need to be introduced into Bermuda.

Some of the contaminated samples collected from the grounding site were pigmented, and large (>1 mm) red particles or 'chips' of antifouling paint could be observed while underwater. In self polishing copolymer AF paints, like

Table 1

Metal concentration (mg/kg dry weight) in surficial sediments collected from sub-tidal sediments around three boat yards in Bermuda (see Fig. 1) expressed together with analytical detection limits and levels recorded in 'control' calcium carbonate sediments collected 60 m from the centreline of the grounding site (data are expressed as mean \pm SD)

	Det.	Control	Boat yard samples								
			Lim	Mean \pm SD	1a	1b	1c	2a	2b	2c	3a
Aluminum (Al)	200	<200	9100	11,900	6700	1700	1700	4000	4800	3200	3400
Barium (Ba)	5	7.8 \pm 4	197	248	287	14	10	14	528	122	395
Chromium (Cr)	0.5	5.4 \pm 0.7	33	36	58	11	11	12	58	63	51
Copper (Cu)	2	2	734	569	630	2100	409	1280	7110	3650	2700
Iron (Fe)	200	1460 \pm 313	23,400	30,700	33,700	6900	3700	2700	32,600	37,300	16,400
Lead (Pb)	5	5.8 \pm 1.8	340	241	1380	248	245	154	493	617	313
Nickel (Ni)	2	<2	12	12	34	<2	<2	7.0	17	50	16
Tin (Sn)	5	<5	14	8.0	19	9.0	8.0	10	41	46	23
Vanadium (V)	1	2.6 \pm 0.5	32	37	39	13	10	9.0	23	16	21
Zinc (Zn)	10	<10	1470	1230	2000	590	150	170	1550	1200	550

Intersmooth 460, biocides are chemically bonded within a copolymer resin. The paint reacts by hydrolysis with seawater releasing the biocide and the surface layer is eroded by moving seawater resulting in the exposure of a fresh, smoother surface, i.e. the paint polishes (self-polishing) (Chambers et al., 2006). While interspersed with bottom sediments the AF paint particles are no longer exposed to moving water (as they are when on the underside of a ship), but abrasion by neighbouring sand particles may also serve to erode the particles' surface and enhance biocide release. In a similar manner, hull cleaning by abrasive products can temporarily double the flux of biocides from AF paints (Schiff et al., 2004). Mechanical weathering of the particles by movement of neighbouring sand grains may also serve to grind larger particles into smaller particles, thereby increasing the surface area for biocide release. Ultimately the AF particles in sediments will probably disintegrate as the hydrolysis/erosion process repeats, the paint layer erodes and the biocide becomes exhausted.

When interspersed with sediments AF paint particles represent a long-term source of toxic biocides and could contribute to the formation of a chemically active boundary layer of freshly released biocide contaminating the interstitial and overlying water column. The particles are also likely to be re-suspended by storms/hurricanes and may land on corals where they will be in direct contact with the surface mucopolysaccharide layer and underlying epithelium. These particles may then kill the underlying coral polyps. For an example of the effect of large AF particle/flakes on coral heads, see Figures 2.3A in Lutz (2006). Some of the re-suspended and re-settled antifouling paint particles may also be ingested by hard corals during normal feeding activities (Mills et al., 2004).

The biocides released from Intersmooth 460 are copper and zinc pyrithione. Copper is released as cuprous ions (Cu^+) which convert rapidly to the cupric ion (Cu^{2+}), which in turn form organic and inorganic complexes and bind to sediments (Morel and Hering, 1993). Copper is exceptionally toxic to corals, inducing dissociation of the coral-algal symbiosis in adult colonies at low (5–50 $\mu\text{g Cu l}^{-1}$) concentrations (Jones, 1997, 2005) and

reducing fertilization success in gametes as low as ~ 10 –20 $\mu\text{g Cu l}^{-1}$ (Heyward, 1988; Reichelt-Brushett and Harrison, 1999). Zinc pyrithione (also known as Zinc Omadine or Zinc 2-pyridinethiol-1-oxide) is used to prevent microbial degradation and deterioration of manufacturing materials. The largest use of ZPT is non-pesticidal (i.e. control of dandruff, seborrheic dermatitis and psoriasis). The mode of action for ZPT includes disruption of cell membranes, disruption of pH-gradients, and complex binding with metals and proteins (Dinning et al., 1998). This leads to disruption of ATP-synthesis and transport through membranes, as well as starvation of metals and other cations in the cell. ZPT has been found to rapidly photodegrade under high UV light (Thomas, 1999) with half lives being reported within minutes (Turley et al., 2000). However, the potential for a transchelation of ZPT to the more stable and more toxic copper pyrithione (CPT), especially when ZPT is used in conjunction with copper in AF paints, means that even in clear tropical water CPT has the potential to accumulate in the sediments (Grunnet and Dahllorf, 2005).

Sediment Quality Guidelines (SQGs) have been used in the past to guide clean up operations following ship groundings. For example Australian ANZECC guidelines were used in the case of the grounding of the *Bunga Teratai Satu* on the Great Barrier Reef (Haynes et al., 2002), where tri-butyl tin contamination was the primary concern. The most relevant SQGs for use in tropical waters are those developed by the Florida Department of Environmental Protection (FDEP, MacDonald et al., 1996) which were derived from NOAA's National Status and Trends Program (NSTP) (see Long and MacDonald, 1998). Within the FDEP SQGs, threshold effects level (TEL) represent concentrations below which adverse biological effects are expected to occur rarely, and the probable effects level (PEL) defines the level above which adverse effects are expected to occur frequently.

Of the 62 samples analysed from the cruise ship grounding site, 44% exceeded the FDEP TEL SQGs for copper (18.7 mg/kg dry weight), and 26% exceeded the PEL (108.2 mg/kg dry weight). Thirteen percent of samples exceeded the zinc TEL (124 mg/kg dry weight) and 6%

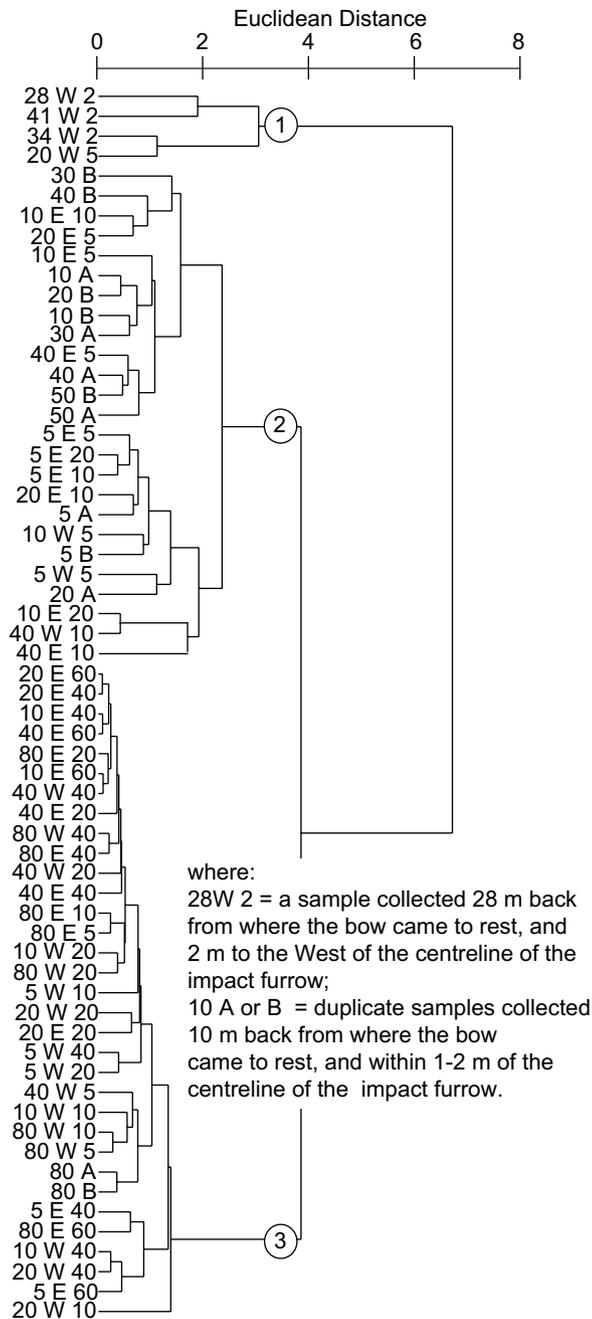


Fig. 4. Dendrogram for hierarchical clustering (using group-average linking) for surficial sediment samples taken from the grounding site of the *Norwegian Crown* cruise ship, calculated on a Euclidean-distance similarity matrix from log transformed metal data.

exceeded the PEL value (270 mg/kg dry weight). All of the clearly contaminated (i.e. red coloured) surficial sediment samples collected from the western side of the impact furrow exceeded the PEL values for copper and zinc respectively and all of the boat yard sediment samples exceeded the copper TEL and PEL values, 75% exceeded the zinc PEL, and all samples exceeded the lead PEL value (112.8 mg/kg dry weight).

Clearly many of the grounding site sediments contain metal concentrations at levels which have the potential to

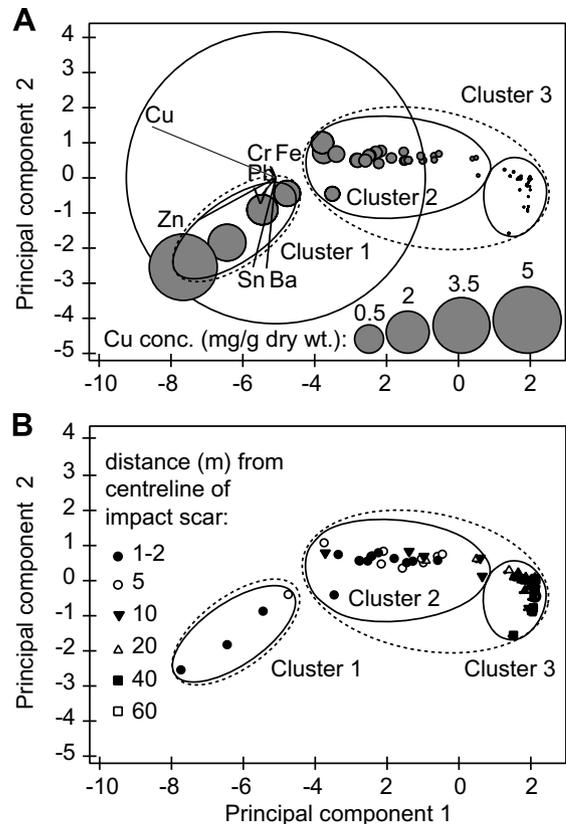


Fig. 5. (A), (B) 2-Dimensional Principal Component Analysis (PCA) ordination of sediment metals levels using group averaged clustering from Euclidean-distance similarities on $\log(x)$ transformed metal concentration data superimposed with similarity levels (see Fig. 4). In (A) bubble plots of copper abundance data are superimposed, where the width of each 'bubble' is proportional to the metal concentration in the respective sediment sample (in mg/g dry weight). In (B) the symbols represent the distance in meters east or west of the impact furrow at which samples were taken and the numbers above the symbols represent the distance along the impact furrow.

be associated with adverse biological effects; however, from an ecotoxicological and risk assessment perspective, the presence of AF paint particles in sediments pose a number of problems including relating chemical contamination levels to bioavailability and hence to environmental effect. The use of SQGs as described above to guide clean-up operation must be conducted carefully. When present as antifouling paint particles, degradation half-life of biocides are extended since much of the biocide is initially bound within the matrix of the paint particle and slowly released through dissolution processes into the sediment (Thomas et al., 2003). If much of the copper or ZPT is associated with the paint particles, as is probably the case in this and other ship grounding incidents, then it may not yet be in a bioavailable form. The FDEP SQGs were not promulgated as regulatory criteria or standards; rather, they were intended, as used here, as informal (non-regulatory) guidelines for use in interpreting chemical data from analyses of sediments and tools for screening sediment quality data to identify priorities for further actions. In this instance, further action should include ecotoxicological studies of the

effects of the antifouling paint contaminated sediment on corals. Similar studies were conducted with sediments from the grounding of the *Bunga Teratai Satu* where the sediments tested exceeded ANZECC sediment guidelines by many orders of magnitude, and resulted in juvenile and adult coral mortality and inhibition of larval settlement and metamorphosis (Negri et al., 2002; Smith et al., 2003).

5. Conclusions

As compared with the gross biological and physical damage caused by a major ship grounding on a coral reef, the insidious contamination of coral reefs by AF paint excoriated from the ship's hull has received very little attention. Much of this contamination will probably be in the form of a spectrum of differently sized AF paint particles interspersed with sediments and these will release their biocides over extended periods. These particles are sometimes visible in the sediments as paint flakes, but often are too small to be seen while underwater. The ecotoxicological effect of these particles is poorly understood, and is in need of further study; nevertheless, their potential for continual slow-release of biocides chosen and designed to prevent settlement of marine organisms, together with movement of sediment contaminated particles around the reef by storms constitutes a significant ecological risk that may serve to undermine the expensive site-remediation activities now associated with major ship groundings. It seems only logical that sampling and assessment for AF paint contamination of grounding site sediments should become part of the detailed evidence collecting procedures, injury assessment, and part of the restoration planning procedures.

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