Passive sampling monitoring of PAHs and trace metals in seawater during the salvaging of the Costa Concordia wreck (Parbuckling Project)

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ABSTRACT

Passive sampling techniques were used for monitoring trace metals and polycyclic aromatic hydrocarbons (PAHs) in the seawater surrounding the Costa Concordia shipwreck (Isola del Giglio, Italy). The monitoring lasted two and a half years (2012–2014) and considered all four phases of the "parbuckling project": stabilisation of the wreckage, installation of steel caissons on both sides of the wreck, parbuckling, and refloating. Dissolved trace metals (Cd, Cr, Cu, Hg, Ni, Pb, and V) were measured with diffusive gradients in thin films (DGT), while freely dissolved PAHs were measured with semi-permeable membrane devices (SPMDs). Passive sampling allowed to detect very low concentrations of contaminants, and indicated significant differences among the sampling stations and among the different steps for salvaging the wreck. The results suggested that the main source of contamination was the heavy working vessel traffic at the disaster site, rather than the release of contaminants from the wreck.

1. Introduction

On the evening of 13 January 2012, the 112,000 tons Costa Concordia cruise ship struck an underwater rock located a few hundred metres east of the Giglio Island coastline (Italy). The ship returned to the island and capsized in shallow water. The hull of the Costa Concordia lay starboard side to the seaward face of a small outcrop near the mouth of the Giglio harbour, resting precariously on the incline to deeper water. Although an environmental disaster of the scale already averted by removing the ship's 2400 tons of fuel shortly after the crash would not occur, the accident immediately raised concerns about the pollution of the once-pristine coastal area, both in terms of the remaining contents of the ship and the long time the wreck would spend in that area before removal. A complex framework of chemical, biological and oceanographic activities (Regoli et al., 2014; Bacci et al., 2016; Casoli et al., 2017; Morroni et al., 2018) was developed to assess the possible contamination events and environmental impact during both emergency operations and wreck salvaging and removal operations. The up-righting of the ship ("parbuckling project"), which ended in July 2014, was the largest and most expensive maritime salvage in history.

This paper presents the results of two and a half years of monitoring the dissolved concentrations of polycyclic aromatic hydrocarbons (PAHs) and trace metals in seawater surrounding the sunken cruise ship through passive sampling, which was conducted during the different parbuckling phases. PAHs were chosen as indicator of pollution produced both by residual fuel inside the wreck than by the activities put in place in the salvage operations. Passive sampling is a reliable

alternative to traditional discrete water sampling methods and allows the measurement of a wide range of contaminants in surface waters (Vrana et al., 2014), including seawater (Schintu et al., 2014). This method could be used to monitor long-term trends, screen contaminants at very low concentrations, and identify sources of pollution. Passive sampling tools carry many advantages, such as: (i) the provision of an integrated measure of contamination over the period of deployment, (ii) the preconcentration of contaminants, which allows a lower limit of quantification (LOQ) than classic analysis of spot samples and (iii) the simplification of the sample matrix. Furthermore, it allows the soluble contaminant fraction to be determined, which is considered the bioavailable fraction (Davison and Zhang, 2012).

Semi-permeable membrane devices (SPMDs) (Huckins et al., 1990) have been used extensively for the screening and source identification of a variety of non-polar organic contaminants, including PAHs in seawater (Komarova et al., 2009; Harman et al., 2009; Marrucci et al., 2013). Diffusive gradients in thin films (DGT) (Davison and Zhang, 1994) are the main PS devices used for monitoring metals in surface waters (Davison and Zhang, 2012).

Despite the growing number of publications on passive sampling over recent decades, field application of the technique has been limited, particularly the parallel use of both organic and inorganic samples. The aim of this study is to evaluate the usefulness of PS techniques for monitoring seawater contamination during the salvaging operations following an environmental disaster.

2. Materials and methods

2.1. Study area and sampling sites

The study area is shown in Fig. 1. Giglio Island (21.2 km^2) lies in the northern part of the Tyrrhenian Sea facing the Argentario Headland, 14 km off the Tuscany coast. Three sampling stations were set up: 1) PN, north of the Costa Concordia wreck in proximity to the stern (42°34502′ N, 10°92,451′ E). Station PN was in a restricted access zone (no recreational activities) that was clearly defined to prevent any disturbance during the wreck removal phases and for safety reasons. 2) ML, outside of the Giglio Harbour (42°35986′ N, 10°92,280′ E). The small harbour of Giglio is enclosed by two piers and contains a brickwork pier where ferries moor. 3) CC, Cala Caldane, a reference site located approximately 2.2 km south of ML (42°34502′ N, 10° 92,451′ E), and not influenced by rescue operations. Nine sampling campaigns were conducted between May 2012 and September 2014, covering all phases of the project (Table 1): 1) Stabilisation: anchoring and stabilisation of the wreck to prevent any slipping or sinking along the steep seabed, 2) installation of submarine supports and portside caissons, 3) parbuckling (or rotation), 4) installation of caissons on the starboard side, and 5) re-floating.

2.1.1. Deployment of the samplers

According to Bergqvist and Zaliauskiene (2007), prior the start of this study, a number of issues were considered, including information on turbulence-flow rates, temperature, conductivity, water depth, and turbidity at the exposure sites. Furthermore, the risks that samplers may be vandalized, stolen or damaged were assessed. The depth of deployment of both SPMDs and DGTs was strongly conditioned by the safety conditions of the yard, which involved a huge number of working vessels and ropes. However, canisters containing SPMDs were deployed below water surface mainly because passive samplers should remain submerged throughout the entire deployment. According to Alvarez (2010), samplers exposed to air during the deployment could be contaminated from airborne chemicals; in addition, it will be impossible estimation of ambient water concentrations as it will not be known how many days the samplers were actually in the water. Furthermore, the aim of this study was not to determine the whole content of PAHs in water, which tends to form a surface film, but their freely dissolved

fraction (Harman et al., 2009). Another reason to deploy SPMDs underwater is the need to avoid photolytic degradation of PAHs (Komarova et al., 2009). Most of the times DGTs were exposed for periods ranging from 14 and 20 days, only two times they stay underwater for 30 days (Table 1). Although long water exposures, no significant biofouling was observed on the diffusive gel, as found by other authors which deployed DGTs in seawater for two weeks periods (e.g. Chen et al., 2017) or even one month (e.g. Murdock et al., 2001; Webb and Keough, 2002; Schintu et al., 2008).

2.2. Chemicals

All solvents were of pesticide analysis grade (Fluka, Milan, Italy). The water was double-distilled and purified. Hydrochloric acid was obtained from J.T. Baker (The Netherlands), while 60% ultrapure-grade nitric acid was obtained from Merck Millipore (Germany). The silica gel was high-purity grade, pore size 60 Å, 70–230 mesh (Fluka, Milan, Italy).

The GPC retention time calibration standards, which were naphthalene (99%, scintillation grade), coronene (95%), sulphur (99.999%), and biphenyl (99%), were obtained from Acros Organics (Geel, Belgium), and bis-(2-ethylhexyl)phthalate was obtained from Sigma-Aldrich (Milan, Italy).

The internal standard, surrogate, and performance reference compounds (PRCs) were as follows: acenaphthylene-d$_8$, fluorene-d$_{10}$, chrysene-d$_{12}$, benzo[e]pyrene-d$_{12}$, pyrene-d$_{10}$, fluoranthene-d$_{10}$ (Chiron AS, Trondheim, Norway), phenanthrene-d$_{10}$, acenaphthene-d$_{10}$, perylene-d$_{12}$, decachlorobiphenyl, and tetrachloro-m-xylene (Ultra Scientific, Bologna, Italy); $^{13}C_{12}$PCB-1, $^{13}C_{12}$PCB-8, $^{13}C_{12}$PCB-37, and $^{13}C_{12}$PCB-54 (Wellington Laboratories, Guelph, Ontario, Canada).

Analytical standard mixtures of PAHs (Naph, Aceph, Ace, Fl, Phen, Ant, Flu, Pyr, BaA, Chr, B(b + j)F, BkF, BaP, BeP, Per, InP, BgP, and DBA) were obtained from Ultra Scientific, Bologna, Italy.

Analytical standard mixtures of branched PAHs (BPAHs; PAH/dibenzothiophenes mixture: N1a, N1b, N2, N3, D0, D1, P1, D2, P2, D3, P3a, Tr, Flu1, P3b, BcP, C1, and C2) were obtained from Chiron AS, Trondheim, Norway.

2.3. PAHs

2.3.1. SPMD preparation, exposure, and retrieval

Standard SPMDs (length 91.4 cm; width 2.5 cm; LDPE wall thickness: 70–95 μm) with 1 mL of 99% purity triolein and PRCs (phenanthrene-d$_{10}$, acenaphthene-d$_{10}$, chrysene-d$_{12}$, fluorene-d$_{10}$, benzo[e]pyrene-d$_{12}$, $^{13}C_{12}$PCB-1, $^{13}C_{12}$PCB-8, $^{13}C_{12}$PCB-37, and $^{13}C_{12}$PCB-54) were purchased from ExposMeter AB, Tavelsjö, Sweden. All deployment devices were cleaned with detergent, tap water, and double-distilled water before being rinsed with acetone and hexane. The SPMDs were transported in sealed clean metal cans and refrigerated at 4 °C. Before transportation by boat, the SPMDs were assembled with proper supports and inserted into stainless steel cages (canisters; ExposMeter AB, Tavelsjö, Sweden). All canisters were rolled in a clean stainless-steel wire net to prevent the PAHs from photodegrading (Komarova et al., 2009), and were sealed in argon for transport. The exposure of the SPMDs ranged from 28 to 70 days. Samplers were deployed at approximately five metres above the seabed, at depths of 25 (PN), 10 (ML), and 24 m (CC). The deployment depth of the canisters (and DGTs) was imposed by the worksite's safety regulations due to the high traffic of boats operating around the wreck. Canisters were hung from a buoy with a 1 cm polypropylene rope and anchored to the bottom with a ballast that weighed approximately 40 kg. After retrieval, the samplers were dismounted. The surface of each SPMD was roughly cleaned with laboratory paper, and each passive sampler was sealed into its corresponding metal can. The SPMDs, field blanks, factory blanks, and spiked SPMDs were cleaned as suggested by Huckins et al. (2006). Each SPMD was immersed in 100 mL of hexane for 30 s. The mounting loop