Cadmium, copper and lead contamination of the seawater column on the *Prestige* shipwreck (NE Atlantic Ocean)

Ricardo Prego*, Antonio Cobelo-García

Marine Biogeochemistry Research Group, Instituto de Investigaciones Marinas (CSIC), 6 Eduardo Cabello Street, E-36208 Vigo, Spain

Received 2 December 2003; received in revised form 24 February 2004; accepted 8 March 2004

Available online 18 May 2004

Abstract

As a result of the *Prestige* tanker sinkage on 19 November 2002, vast amounts of heavy fuel were dumped from the shipwreck lying on the bottom to the surface of the NE Atlantic Ocean. The heavy metal contamination of the water column was studied from 4–8 December 2002 taking advantage of an opportunistic cruise onboard the R/V *Atalante*. Clean laboratory procedures were used in order to analyse 32 water samples and two heavy fuel samples (cargo tanker and surface seawater of the shipwreck area) by means of differential pulse anodic stripping voltammetry and electrothermal atomic absorption spectrometry. Around 25 kg of Cd, 170 kg of Cu and 10 kg of Pb were released into the ocean water over seventy days of which 2% (Cd), 23% (Cu) and 71% (Pb) remain in the floating fuel patches on the sea surface. In the *Prestige* shipwreck area, where the seawater was free of oil patches, copper (2.8–8.5 nM) and lead (0.10–0.78 nM) contamination was only observed in the uppermost ocean layer, from 100 m depth for copper and the top ocean for lead. On the contrary, the cadmium levels (0.02–0.41 nM) observed were within typical or uncontaminated values.

© 2004 Elsevier B.V. All rights reserved.

Keywords: Cadmium; Copper; Lead; Seawater; Contamination; Oil spill; Heavy fuel; *Prestige* tanker

1. Introduction

On 19 November 2002, the *Prestige* oil tanker broke into two pieces in the waters of the Northeast Atlantic Ocean. The stern sank at 11:45 h, with approximately 25,900 t of heavy fuel at the 42°12.6′N, 12°03.0′W coordinates. Several hours later, the bow also sunk (16:00 h, at 42°10.8′N, 12°00.6′W) with 37,900 t of heavy fuel [1]. Several days later, the fuel that spilled into the sea surface when the ship broke began to reach the coast of Galicia (NW Iberian Peninsula) transported by the sea drift. Satellite pictures taken at that time showed new vast oil patches covering an extensive area around the shipwreck [2]. The fuel was emerging from the bow and stern tanks at the sea bottom (3,819 m depth, 42°10.6′N, 12°03.8′W and 3,530 m depth, 42°12.4′N y 12°02.9′W, respectively). Then Sociedad Española de Salvamento y Seguridad Marítima (SASEMAR) planned the *Prestinaut* campaign in order, among other aims, to evaluate the potential fuel contamination of the seawater.

The heavy fuel oil transported by the *Prestige* was classified as n° 6, i.e., a black distillation-tower residuum diluted with 5–20% distillate [3]. This type of fuel usually contains several metals, which may vary depending on the crude source, because they are concentrated during the fractional distillation of petroleum. In general, a maximum concentration of certain elements such as cadmium (<1 μg g⁻¹), or lead (2 μg g⁻¹) can be considered [4]. This was confirmed for the oil transported by the *Prestige*, from the metals analysis of the fuel–seawater emulsion deposited on the Galician littoral [5], as was the case to Cu (1–10 μg g⁻¹), Cd and Pb (sub-μg g⁻¹ range) [6].

In general, the land-ocean inputs are the main source of the heavy metal fluxes and sea contamination, and this is the case for the Galician coastline [7]. Also, in the oil tanker accidents, the coastal areas are the most affected because the shipwreck usually occurs within the continental shelf [8]. However, no studies were carried out in previous catastrophes to evaluate the impact of these oil spills on metals contamination, as in the recent example the *Baltic Carrier* tanker off the Danish coastline [9] (April 2001) with the same type of heavy fuel as the *Prestige*. Only on the coast of Kuwait, the release of metals from the oil split during the...
Gulf War has been pointed as one of the major causes of the coastal contamination of metals [10]. Thus, research on metal concentrations and distribution in oceanic areas impacted by tanker accidents is very scarce. For this reason, the heavy metal contamination in the seawater column was opportunistically surveyed 12 days after the Prestige wrecking, taking advantage of the cited short Prestinaut cruise.

2. Materials and methods

Two sets of samples were collected in the seawater column vertically over the Prestige tanker wreckage (42°11′N, 12°02′W) from 4–8 December 2002 during the Prestinaut cruise. The first set (Table 1) was taken from the R/V Atalante at four stations at 0, 5, 10, 20, 50, 100 and 190 m depth where the sea surface was free of oil spill patches. Moreover, one sample of the floating fuel (non-emulsified) on the seawater surface was taken. The second set (Table 1) was sampled from the Nautile manned submersible in the bottom waters close to where the bow and stern of the tanker lie, at four different immersions (3530–3820 m depth), three of them at less than 5 m from the tanker and one at 100 m above the bow. Immediately after the arrival of the hydrographic bottles onboard, samples were taken for the determination of Cd, Cu and Pb using new low-density polyethylene bottles (500 ml). Those bottles were previously acid-washed (10% nitric acid) for a week, rinsed (five times) with Milli-Q50 water acidified to pH 2 using 65% HNO3 (Merck Suprapur) and stored in zip-lock plastic bags. Just before taking the samples, the bottles were emptied and rinsed with the sample; once having taken the samples, the bottles were again packed in zip-lock plastic bags. At the onshore ‘clean’ laboratory, the samples were thawed and acidified—using 65% HNO3 (Merck Suprapur)—to pH 3 pending analysis. Samples of the floating fuel, together with a sample from the original cargo of oven (Milestone 1200 Mega), in accordance with the Milestone digestion procedure for oil samples. Samples, including five blanks, were diluted to 25 ml using polypropylene volumetric flasks and stored in a refrigerator at 4 °C until analysed. Cd, Cu and Pb were determined by electrothermal atomic absorption spectrometry (ET-AAS) in a Varian 220 apparatus equipped with Zeeman background correction using the method of standard additions.

The determination of Cd, Cu and Pb in the water column was carried out by differential pulse anodic stripping voltammetry (DPASV) using a 745 VA trace analyser (Metrohm) attached to a 695 Autosampler (Metrohm). Prior to the determination, samples were digested for 1 h using a 705 UV digestor (Metrohm). In order to avoid the contamination of samples, the complete analytical procedure was undertaken inside a ‘clean’ laboratory and clean techniques were used throughout the analytical procedure. Blanks for the analytical procedure—one blank every five samples—were run. The results presented are blank-corrected. The accuracy of the analytical procedure was checked using two certified reference materials: CRM-403 (North Sea water; BCR, Community Bureau of Reference) and CASS-4 (Coastal Seawater; NRC, Canada), obtaining good agreement with the certified concentrations, as shown in Table 2.

3. Results and discussion

Vertical profiles of cadmium, copper and lead in the surface oceanic layer (0–200 m depth) of the Prestige shipwreck

Table 1: Station data, code, coordinates and depth levels in the oceanic column for the seawater and heavy fuel samples taken from the R/V Atalante (A) and the Nautile manned submersible (N) in the area of sunken the oil tanker

<table>
<thead>
<tr>
<th>December 2002 (day)</th>
<th>Station code</th>
<th>Latitude (°)</th>
<th>Longitude (°)</th>
<th>Levels (depth, m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>02</td>
<td>A-1</td>
<td>42°14.30′</td>
<td>12°03.78′</td>
<td>0–5–10–20–50–100–190</td>
</tr>
<tr>
<td>02</td>
<td>A-2</td>
<td>42°10.35′</td>
<td>12°04.18′</td>
<td>0–5–10–20–50–100–190</td>
</tr>
<tr>
<td>02</td>
<td>A-3</td>
<td>42°12.50′</td>
<td>12°03.16′</td>
<td>0–5–10–20–50–100–190</td>
</tr>
<tr>
<td>02</td>
<td>N-1</td>
<td>42°12.48′</td>
<td>12°03.25′</td>
<td>3715 (100 m above bow)</td>
</tr>
<tr>
<td>02</td>
<td>N-2</td>
<td>42°12.60′</td>
<td>12°03.60′</td>
<td>3800 (5 m above bow)</td>
</tr>
<tr>
<td>02</td>
<td>N-3</td>
<td>42°12.36′</td>
<td>12°02.92′</td>
<td>3510 (3 m above stern)</td>
</tr>
<tr>
<td>02</td>
<td>N-4</td>
<td>42°12.36′</td>
<td>12°02.92′</td>
<td>3510 (3 m above stern)</td>
</tr>
</tbody>
</table>

Surface water was free of oil patches for A-1, A-2 and A-3 stations, but there were some fuel patches in A-4.
Total Pb Concentration (pM)

0 150 300 450 600 750 900 2000

Depth (m)

0 25 50 75 100 125 150 200

St. A-1
St. A-2
St. A-3
St. A-4

Fig. 1. Seawater column profiles (0–190 m depth) of total metal concentrations at four stations in the ocean area of the Prestige shipwreck. Black broken lines represent the typical metal levels for surface layer (0–200 m) in the Northeast Atlantic waters.

Table 3

<table>
<thead>
<tr>
<th>Depth (m)</th>
<th>Cd</th>
<th>Cu</th>
<th>Pb</th>
</tr>
</thead>
<tbody>
<tr>
<td>0–5</td>
<td>0.16±0.02</td>
<td>8.5±2.8</td>
<td>0.78±0.10</td>
</tr>
<tr>
<td>50–190</td>
<td>0.16±0.02</td>
<td>3.1±0.9</td>
<td>0.26±0.05</td>
</tr>
<tr>
<td>350–3820</td>
<td>0.42±0.15</td>
<td>3.1±1.7</td>
<td>0.10±0.03</td>
</tr>
<tr>
<td>Natural values</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0–200</td>
<td>0.19±0.02</td>
<td>2.0±0.6</td>
<td>0.22±0.03</td>
</tr>
<tr>
<td>500–4500</td>
<td>0.40±0.20</td>
<td>3.5±1.5</td>
<td>0.15±0.05</td>
</tr>
</tbody>
</table>

As a reference, the metal levels in pristine surface and deep seawater of NE Atlantic are also shown.

Ranges of metal concentrations (nM) measured in the oceanic area of the Prestige shipwreck.

Table 4

<table>
<thead>
<tr>
<th>Depth (m)</th>
<th>Cd</th>
<th>Cu</th>
<th>Pb</th>
</tr>
</thead>
<tbody>
<tr>
<td>PF</td>
<td>0.49±0.11</td>
<td>3.39±0.31</td>
<td>0.21±0.02</td>
</tr>
<tr>
<td>A-f</td>
<td>0.03±0.01</td>
<td>0.79±0.14</td>
<td>0.15±0.02</td>
</tr>
</tbody>
</table>

Errors in the determinations represent one standard deviation. Seven replicates were analysed.

Fig. 1. Seawater column profiles (0–190 m depth) of total metal concentrations at four stations in the ocean area of the Prestige shipwreck. Black broken lines represent the typical metal levels for surface layer (0–200 m) in the Northeast Atlantic waters.

area are shown in Fig. 1. Cd showed very similar results at the four stations and the concentrations obtained lie within the typical values previously reported for this area of the Northeast Atlantic [11–13]. This same situation also applies for Pb, with the exception of the concentrations found in the uppermost layers where the concentrations found were from 3 to 15 times higher than ‘pristine’ values [14,15]. The increase of Cu concentrations in the upper layers was not so pronounced, around six times higher than ‘pristine’ values [11–13]; however these enhanced concentrations with respect to typical values were observed down to 50 m depth. Typical or ‘pristine’ values for the NE Atlantic waters together with the metal concentrations measured in this study are indicated in Table 3. Although no oil patches were detected visually, concentrations of Cu and Pb in the uppermost layers were up to eight times higher than previously reported concentrations [11,14,16]. There was a down column decrease on metal concentrations (50–200 m depth) tending to typical (uncontaminated) values below 10 m depth in the case of lead and 100 m depth for copper.

The rubble of the tanker lies in the Northeast Atlantic Deep Water (NEADW), which is a homogeneous water mass (salinity: 34.89–34.92, temperature: 2.52–2.58 °C; [17]), where the typical metal concentrations (Table 3) are in the range of the values of Cd, Cu and Pb observed in this study. Therefore, no contamination by these metals in the bottom waters close to the bow and the stern of the Prestige rubble was detected. Cadmium, copper and lead concentrations in the seawater column present non-significant correlations between them.

The results point out that these high concentrations of metals arise from the Prestige shipwreck on the sea bottom. Regarding Table 4, the fuel contained elements and they were lost, during fuel rise from the shipwrecked tanks to the sea surface. The metal concentration in fuel is known (Table 4) and it may be observed that an important part of the Cu (77%) and practically all its Cd content was lost since the floating oil is deficient in Cu (0.8 μg g⁻¹) and Cd.
It is known that, when the bow and stern of the Prestige sank, their tanks contained 63,800 t of fuel. These tanks were spilling oil until 28 January 2003, when most of the leaks were sealed [18]. The Prestige wreckage still held 13,800 t of fuel (13,100 t in the bow and 700 t in the stern) in September 2003 [19]. In accordance with these values and the metals concentrations in the cargo and floating fuel shown in Table 4, ca. 24 kg of Cd, 130 kg of Cu and only 3 kg of Pb was released into the seawater over 70 days; while in the floating fuel patches there still remain 1 kg of Cd, 40 kg of Cu and 7 kg of Pb. These metal inputs could be considered as unimportant if they are compared with the land-based fluxes to estuarine systems, e.g. copper in the Pontevedra Ria [20]. Nevertheless, the low metals concentration in the oceanic environment [14] and the levels measured here, a short time after the Prestige accident, indicates that heavy metal contamination occurred in the Northeast Atlantic Ocean.

4. Conclusion

Contamination by copper and lead was observed in the uppermost layer in the Prestige shipwreck area of the Northeast Atlantic Ocean. This contamination was not detected for cadmium nor for the three surveyed metals in the bottom seawater above the bow and stern of sunken Prestige. In general, this type of contaminant, where the fuel is spilled from the rubble of sunken ships, should be considered in future studies. At present, little attention has been paid to the metal contamination of natural waters by oil spills, despite the fact that this was already reported to be a source of metals to the environment. The possibility of contamination by copper, lead and other metals need to be studied in future oil spill events.

Acknowledgements

The authors would like to thank for their kind cooperation during sampling, Mr. W. Redondo, Captain G. Ferrand and the crew of R/V Atalante, and Mr. N. Compagnot, responsible of the manned submersible Nautile. Prof. J. Albàigés is also acknowledged for the fuel sample of the original tanker cargo, Prof. F.F. Pérez for his information on the cruise, and Ms. A. Labandeira for the ET-AAS analysis. Finally, we wish to express our gratitude to SASEMAR for letting us work in the early prospecting campaign.

References