Marine Pollution Bulletin 60 (2010) 998–1004

Contents lists available at ScienceDirect

Marine Pollution Bulletin

journal homepage: www.elsevier.com/locate/marpolbul

A study of marine pollution caused by the release of metals into seawater following acid spills

Jean-Yves Cabon[a], Philippe Giamarchi[a,*], Stephane Le Floch[b]

[a] Université Européenne de Bretagne, Université de Brest, UMR CNRS 6521 CEMCA, 6 av. Le Gorgeu, 29238 Brest Cedex 3, France
[b] Cedre – 715, Rue Alain Colas/CS 41836 – 29218 Brest Cedex 2, France

ARTICLE INFO

Keywords:
Trace metals
Pollution
Marine sediment
Seawater
Acids

ABSTRACT

This study examined the potential metal pollution induced by the accidental spill of different acids into seawater. The acids sink to the bottom according to their densities and subsequently react with marine sediments. The acids selected for this study were acetic, hydrochloric, nitric, sulfuric, and phosphoric acids; the metallic elements selected were Cr, Cu, Fe, Mn, Pb and Zn. The sediment was collected in Brest Harbour. The percentages of metals released from this sediment in the presence of various concentrations of acids in seawater were important; concentrations of approximately 7 mg L^{-1} for Mn and 60 mg L^{-1} for Zn were observed under our experimental conditions. We also examined the rate of release of these metals from the sediment into the seawater in the presence of the different acids and under different experimental conditions. We found that most of the metallic elements were released from the sediments into the seawater during the first fifteen minutes of exposure. After this time, a high degree of pollution was induced if acids leached into seawater were not rapidly diluted.

1. Introduction

Acids are chemical substances that are transported in large quantities by ship. Each year approximately 800,000 tons of phosphoric acid, 770,000 tons of sulfuric acid, and 650,000 tons of acetic acid are transported through European harbors. Recent accidents have occurred, such as the wreck of the "ECE" (a Marshall Islands registered chemical tanker) in 2006, which was carrying 10,000 tons of phosphoric acid, and the wreck of the "Balu" (a Maltese chemical tanker) in 2001, which was carrying 8000 tons of sulfuric acid (Marchand, 2003; HELCOM, 2002).

These major oceanic spills have direct and immediate effects on aquatic life through significant decreases in pH and increases in temperature and through the production of toxic gases. Following these immediate effects, another type of pollution occurs as the acids interact with the sediments. These effects are especially pronounced if the accidents occur in a harbor or an estuarine area in which the marine currents are weak, which induces a slow dilution of acids in seawater. Metals are present in sediments with different physico-chemical forms (labile, carbonate, sulfate, sulfur, organic, etc.) and are released into the marine environment at varying rates (Marin et al., 1997; Petronio et al., 2000; Morel and Price, 2003; Hirose, 2006). The release of the acid from the sediment into the seawater depends on the nature of the acid that was spilled and the concentration of the acid in seawater when it was leached into the sediment.

Modeling the effects of acid spills is nearly impossible owing to the number of parameters to be considered, such as the quantity of acid, the flow of acids out of the ship, the ship depth, the depth of the water column, wind, waves, marine currents, the nature of the acid, the tide coefficient, the nature and granulometry of the sediment, the metal concentration, the sample homogeneity and the release kinetics. Therefore, the only way to study acid spills is to follow the consequences of a real event and to try and highlight trends that will allow improvements to be made in the protocol following future accidents.

The objective of this study was to attempt to evaluate some of the environmental effects of an accidental spill of a large quantity of acid in seawater and of the potential reaction of the acid with sediment. In particular, we examined the release of metallic elements into the marine environment and the influence of different concentrations of acetic, hydrochloric, nitric, sulfuric, and phosphoric acids on the release of metals from a sediment collected in Brest Harbour. We studied the behaviors of metals that are either essential, neutral or toxic to marine life, including chromium, copper, iron, manganese, lead and zinc (Comber et al., 2008; Langston, 1990; Barka et al., 2000). Furthermore, we investigated the release of these metals from sediments in the presence of different concentrations of acids, both with and without agitation and for different periods of contact.

---

[*] Corresponding author.
E-mail address: philippe.giamarchi@univ-brest.fr (P. Giamarchi).

0025-326X/$ - see front matter © 2010 Elsevier Ltd. All rights reserved.
doi:10.1016/j.marpolbul.2010.02.002

2. Materials and methods

2.1. Sediment

The sediment (~1 kg) used in this study was collected in Brest Harbour. The sediment was dried at 100 °C and then manually crushed with a mortar, passed through a 500 μm sieve and vigorously shaken to obtain a homogeneous sample, allowing for repeatable results with small sediment masses (0.2 g).

2.2. Chemicals

Hydrochloric, nitric, sulfuric, phosphoric and acetic acids were obtained from Merck products. Standard solutions of Cr, Cu, Fe, Mn, Pb and Zn were used to produce calibration curves (1 g L^{-1} in 0.5 M HNO_3, Merck solutions). The characteristics of these solutions are provided in Table 1. All dilutions were prepared in Milli Q water (18.2 MΩ cm^{-1}). Seawater was pumped from Brest Harbour at the Cedre study site.

2.3. Leaching procedure

Each of the different acid solutions (20 mL) was added to 0.2 g of sediment in 30 mL Teflon flasks. For each acid, a total of 10 repetitions were used, and ten flasks were shaken simultaneously for 15 h at room temperature using a mechanical KS 130 basic IKA shaker at a speed of 60 rpm. After decantation, 1 mL of the supernatant was obtained with a pneumatic syringe and diluted to 100 mL with 0.1 M HNO_3. For kinetic studies, 100 mL of the different acid solutions were added to 1 g of sediment in a Teflon flask; 2 mL of the sediment slurry was filtered with a pneumatic syringe to separate the sediment from the solution before the solution was diluted with water (0.45 μm Sartorius membrane filters).

2.4. Total digestion of sediment

Concentrated acid (5 mL) and concentrated HF (2 mL) were added to 0.2 g of dry sediment in a Teflon flask. After any effervescence had disappeared, the flask was heated on a Stuart block heater at 100 °C overnight, and 2 mL H_2O_2 were added and warmed at 85 °C for 2 h. The acid solutions were then evaporated to dryness, and this procedure was repeated three times. Then, 5 mL of HNO_3 were added and the flasks were heated at 100 °C for 2 h. The solution was then diluted with water to make up a 100 mL solution before metal analysis was conducted using graphite furnace atomic absorption spectrometry (GFAAS).

2.5. Organic matter content

The organic matter content (% dry sediment) was determined by charring at 450 °C for 24 h.

2.6. Determination of metals by GFAAS

The metal concentrations in the different solutions were determined by graphite furnace atomic absorption spectrometry. A Perkin–Elmer SIMAA 6100 was used in the single element monochromator mode for all atomic absorption measurements. Metals were analyzed in end-capped pyrolytic coated graphite tubes equipped with integrated platforms. Argan was used as the inert gas during processing. Samples were delivered to the furnace using a Perkin–Elmer AS-800 auto-sampler and were stored in acid washed polypropylene cups prior to injection. The light sources were Perkin–Elmer hollow cathode lamps. Calibration curves were produced and, when necessary, solutions were diluted before measurements were taken. Dilutions were carried out with calibrated Gilson Pipetman pneumatic syringes. To determine the concentrations of Cr, Cu, Fe and Mn, a 2300 °C atomization temperature was used; for Pb and Zn, a 1800 °C atomization temperature was used. Furnace programs have been optimized previously (Cabon et al., 2007; Salomon et al., 2000; Le Garrec et al., 1997, 1998). No pretreatment step was used for the determination of metals in these different solutions. Pd (10 μg Pd), introduced as $Pd(NO_3)_2$, was used as the chemical modifier in all measurements.

Table 1
Acid characteristics and observed effects after mixing with seawater (1/1).

Acid	HNO_3	HCl	H_3PO_4	H_2SO_4	AcOH
Solution at (%)	65	32	85	98	100
Density	1.39	1.16	1.7	1.8	1.05
Temperature reach after seawater mixing (°C)	35	33	25	102	20
Observations after mud mixing (°C)	Moss	Moss	Moss	Moss	
	21	20	21	34	20
	No color	Yellow	Brownish	Brown	Brown

3. Experimental results

3.1. Determination of the metal contents of sediments

The total metal content in the sediment sample was determined after being digested in the HNO_3-HF medium. The total mass fractions of metals in the sediment sample are presented in Table 2. Metal mass fractions of different types of reference sediments produced by the National Research Council of Canada are also presented in this Table. This table clearly indicates that our sediment is heavily contaminated, particularly with lead, copper and zinc. These metals can be toxic to marine life if they are released quickly into seawater in large quantities.

3.2. Physico-chemical characteristics of acid-seawater mixing

As shown in Table 1, when acids are mixed with sea water (1/1 volume to volume), an increase in the temperature of the acid solution is observed. This increase in temperature depends on the nature of the acid and is particularly high for sulfuric acid, which produces a temperature of approximately 100 °C. When non-diluted acids are mixed with the sediment, the carbonate and sulfide contents of these acids generate gases such as CO_2 and H_2S, which induces the formation of moss. A change in the coloration of the acid solutions through the formation of corresponding metallic complexes and the liberation of organic substances was also observed (Table 1). The total organic content was found to be approximately 10% of the dry sediment mass.

Acids sink in seawater at varying rates depending on their density; consequently, acids are diluted with seawater to varying degrees before being leached into the sediment. The dilution of these acids in seawater is also dependent on the depth of the water column and on the mixing conditions of the environment.

Table 2
Fraction of metal mass in different sediments (μg/g).

	Cr	Cu	Fe	Mn	Pb	Zn
HISS-1	30	2.29	2460	66.1	3.13	4.94
MESS-3	105	33.9	43,400	324	21.1	159
PACS-2	90.7	310	40,900	440	183	364
Our sediment	76	700	14,400	260	500	1160
HISS-1		Collected from the Hibernian Shelf, off the coast of Newfoundland				
MESS-3		Collected from the Beaufort Sea				
PACS-2		Collected from Esquimault Harbour, B,C				