Marine Chemistry 185 (2016) 65–73

Contents lists available at ScienceDirect

Marine Chemistry

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

Distribution and geochemical behaviour of antimony in the Gironde Estuary: A first qualitative approach to regional nuclear accident scenarios

Teba Gil-Díaz [a], Jörg Schäfer [a,*], Frédérique Pougnet [a], Melina Abdou [a], Lionel Dutruch [a], Frédérique Eyrolle-Boyer [b], Alexandra Coynel [a], Gérard Blanc [a]

[a] Université de Bordeaux, UMR CNRS 5805 EPOC, Bat 18, Allée Geoffroy Saint-Hilaire, 33615 Pessac, France
[b] Laboratoire de Recherche sur les Transferts dans l'Environnement, Institut de Radioprotection et de Sûreté Nucléaire (IRSN), PRP-ENV/SERIS/LRTE, Centre de Cadarache, bat 159, 13115 St Paul lez durance, France

ARTICLE INFO

Article history:
Received 15 October 2015
Received in revised form 8 February 2016
Accepted 9 February 2016
Available online 10 February 2016

Keywords:
Antimony
Salinity gradient
Distribution coefficient
Residence time

ABSTRACT

Antimony (Sb) is a highly toxic trace element for which environmental biogeochemical cycles are still relatively poorly known, especially in coastal aquatic systems. In addition, Sb is a fission product in nuclear power plants (NPPs), presenting non-negligible decay and consecutive exposition rates over short to mean terms (*i.e.*, ^{125}Sb isotope: half-life of 2.76 years). Understanding the environmental behaviour and fate of natural stable isotopes and combining this with intrinsic properties of the respective radionuclides (*e.g.* half-life) is essential to predict the environmental fate and potential dispersion of radioisotopes before accidental NPP events. In the present work, the distribution and geochemical behaviour of stable Sb are determined for the first time in the highly turbid Gironde Estuary. Both dissolved and particulate concentrations along the estuarine salinity and turbidity gradients were quantified during low, intermediate and high freshwater discharges. Results clearly suggest that long residence times within the salinity and turbidity gradients favour the observed non-conservative, additive behaviour of Sb. Distribution coefficients ($\log_{10} K_d \approx 3.5–4.4$ l kg^{-1}) indicate that in the Maximum Turbidity Zone (MTZ; SPM ~1000 mg l^{-1}) ~90% of total Sb occurs in the particulate phase, compared to only ~10% in the less turbid portions of the estuary (SPM ≤ 100 mg l^{-1}). We propose a first/broad qualitative approximation (scenarios) to possible behaviour and dispersion of Sb radionuclides in case of accidental release from the Blayais NPP located on the Gironde Estuary. Our results suggest that the hydrological situation and the position of the MTZ during a potential accident can be primordial to residence time and distribution pathways in the estuary. We estimate that (i) high river discharge and a downstream position of the MTZ may favour Sb radionuclide adsorption onto particles, implying long (months to years) residence times in the estuary and a high risk of seasonal upstream transport into the city of Bordeaux, whereas (ii) under low discharge conditions, dissolved Sb species will predominate implying rapid transport and higher dispersion along the coast.

1. Introduction

The Fukushima Dai-ichi Nuclear Power Plant (FDNPP) event in Japan (11th March 2011) has raised worldwide new questions and doubts concerning nuclear safety and possible accidental impacts on the oceanic environment. The direct and massive contamination of seawater used for urgency reactor cooling and the huge leakages of radioactive seawater were not foreseen as a likely scenario. As a consequence, the French National project AMORAD (ANR-11-RSNR-0002) was initiated in 2013 to unveil means for accurate evaluation of radioactive contamination on humans and environmental compartments at high spatiotemporal resolution (*http://www.irsn.fr*). In France ~75% of the total power supply depends on locally produced nuclear energy in 19 NPPs mostly located in the coastal French Metropolitan territory (WNA, 2015). After NPP accidents, the largest inventory among radionuclides released and followed up is mainly dominated by volatile fission products such as noble gases (xenon, Xe, and krypton, Kr), iodine (I) and caesium (Cs) isotopes (Korsakissok et al., 2013; Steinhauser et al., 2014; Thakur et al., 2013; Ueda et al., 2013). However, there are other radioactive elements for which behaviours are unknown although their ranges of action and relevance can be equally important depending on the accidental conditions. In addition, current radionuclide studies are accident-dependent, thus performed after NPP fallout events. This

* Corresponding author.
E-mail addresses: teba.gil-diaz@u-bordeaux.fr (T. Gil-Díaz), jorg.schafer@u-bordeaux.fr (J. Schäfer), frederique.pougnet@u-bordeaux.fr (F. Pougnet), melina.abdou@u-bordeaux.fr (M. Abdou), lionel.dutruch@u-bordeaux.fr (L. Dutruch), frederique.eyrolle-boyer@irsn.fr (F. Eyrolle-Boyer), alexandra.coynel@u-bordeaux.fr (A. Coynel), gerard.blanc@u-bordeaux.fr (G. Blanc).

http://dx.doi.org/10.1016/j.marchem.2016.02.002
0304-4203/

clearly limits our knowledge on their environmental dispersion, persistence and fate to very few case studies, leaving very high uncertainty in dispersion scenarios and risk assessment. Stable isotopes and radionuclides of the same chemical element are commonly accepted to have analogous, or at least have proportional, chemical behaviour (*e.g.*, solubility, speciation, *etc.*; IAEA Report-422, 2004; Yang et al., 2012). Therefore, studies on stable isotopes improve our understanding of the environmental behaviour of their radioactive analogues, without them being present in the environment.

Antimony (Sb) has a high relative significance among the fission products in NPP with non-negligible radioactivity at relatively medium (<30 years) exposure terms after the irradiation event (Akatsu et al., 1974; Delacroix et al., 2002). Its isotopes are produced with a probability of ~8% from ^{235}U fuel and ~7% from ^{239}Pu in less than 24 h both by direct fission and by decay of other fission products, which is similar to the fission yields for Cs and I isotopes (9–12%; calculations obtained from information in Sonzogni, 2013 and Element Collection Inc., 2007). The isotope with highest half-life (^{125}Sb; $T_{1/2}$ = 2.76 years) was emitted by both the Chernobyl (ChNPP, Ukraine 26th April 1986) and the FDNPP accidents (Steinhauser et al., 2014; Thakur et al., 2013). Moreover, ^{125}Sb was detected in molluscs (Whitehead et al., 1988) and soils (Carbol et al., 2003; Papastefanou et al., 1988) as early as one month and up to 6.5 years after the ChNPP accident, respectively. These measurements reflect the importance of Sb radioisotopes dispersion for direct (through skin contact and/or inhalation) and/or indirect (through food supplies) human exposure.

The study of stable Sb, considered a pollutant of priority interest by the European Community (Directive 2006/11/EC), the German Research Council (DFG, 2012) and the U.S. Environmental Protection Agency (USEPA, 2013), was largely neglected until recently (Filella et al., 2002a; Smichowski, 2008). Increasing concern on Sb in the last decade has been related to its high contamination levels in certain areas, jeopardizing public health. Current studies have focused on Sb determination in atmospheric aerosols (Smichowski, 2008), its removal from contaminated waters and wastewaters (Ha et al., 2009; Ungureanu et al., 2015) and its mobility in different soils and crop uptake (Pierart et al., 2015; Wilson et al., 2010; Zhang et al., 2014). Additionally, Sb quantification methods and speciation in a wide range of environmental matrices at trace and ultratrace levels have been reviewed (Ferreira et al., 2014; Nash et al., 2000; Smichowski et al., 1998; Smichowski, 2008), confirming its ubiquity in the environment (Asaoka et al., 2012; Filella et al., 2002a; Filella, 2011; Silva et al., 2014; Ungureanu et al., 2015; Wilson et al., 2010). Nevertheless, the integration of all this data into a general biogeochemical cycle has not yet been accomplished (Filella et al., 2009) and there is still a lack of knowledge on the chemical processes involved in environmental Sb behaviour, transformation and transport (Filella, 2011), especially in advective flow systems (Zhang et al., 2014).

The aim of this study is to characterize the distribution and geochemical behaviour of Sb within the Gironde Estuary in order to evaluate Sb radionuclide behaviour and dispersion within the estuary and the coastal ocean, in case of an accidental release from the Blayais NPP (inside the Gironde Estuary). To achieve this, specific objectives are to (i) provide the first data on Sb dissolved and particulate concentrations and Sb partitioning along the turbidity and salinity gradients of the Gironde Estuary and (ii) to propose a preliminary qualitative conceptual model (scenarios) for the Gironde estuarine system to predict potential dispersion in case of accidental Sb radionuclide emissions from the Blayais NPP.

2. Material and methods

2.1. Study area

The Gironde Estuary is the largest estuary in SW Europe with a total surface area of 635 km^2 at high tide and a watershed size of approximately 81,000 km^2 (Salomon, 2002). The geographical limit of the estuary is at the confluence of the Garonne (average discharge, Q = 594 m^3 s^{-1}) and Dordogne (Q = 318 m^3 s^{-1}) rivers. However, the marine influence (*i.e.*, semidiurnal tidal cycle of 12 h 25 min) extends 180 km upstream from the estuary mouth, defining the limit of the dynamic tide at La Réole on the Garonne River (Kilometric Point: KP −70, Fig. 1). The residual circulation (caused by the salinity-driven vertical gradients) and the hypersynchronous character of the estuary develop a Maximum Turbidity Zone (MTZ) with Suspended Particulate Matter (SPM) concentrations >1 g l^{-1} (Sottolichio and Castaing, 1999). The MTZ is mostly found in the low salinity region and migrates up and down the estuary at both seasonal (dependent on river flow) and tidal time scales (Sottolichio and Castaing, 1999). This implies that low river discharge conditions (typical of summer seasons) favour the entrance of seawater further upstream in the estuary, causing the MTZ to reach the city of Bordeaux (Sottolichio and Castaing, 1999). Drought periods have increased in intensity and duration over the past decades due to overall decrease in annual average freshwater supply to the Gironde Estuary, favouring the saline intrusion upstream of Bordeaux (Etcheber et al., 2011; Sottolichio et al., 2011). In particular situations (generally 10–20 days per year), the MTZ can be partly flushed outside of the estuary when specific conditions are met: continuous and high river discharge during weeks with high tidal coefficient (Castaing and Allen, 1981). The SPM has an average residence time in the estuary of 1–2 years (Castaing and Jouanneau, 1979), whereas the water residence time varies from 86 days in low discharge conditions to ~18 days under high discharge conditions (Castaing and Jouanneau, 1979; Jouanneau and Latouche, 1981).

Ore deposits and former mining areas in the upper reaches of the Garonne and Dordogne watersheds (Massif Central and the Pyrenean Mountains; Fig. 1) are major sources of many metals and metalloids to the Gironde Estuary, including the oxyanion-forming Sb (BRGM, 2014; Masson et al., 2009, 2011). Moreover, anthropogenic point sources of Sb linked to former power station landfills and several industrial tailings (ore treatment, coal mine) have also been identified in the Lot-Garonne River system (Coynel et al., 2007a, 2007b, 2009).

The Gironde Estuary watershed hosts two NPPs. The Golfech NPP is located on the Garonne River ~160 km upstream from Bordeaux and the Blayais NPP directly next to the estuary in the area of Braud-et-Saint-Louis at 48 km NNW of Bordeaux. During the past 2 decades a series of incidents have occurred in both NPPs, and were attributed to the levels 1 and 2 of the International Nuclear Event Scale (http://france.edf.com/).

2.2. Sample collection

Water samples were collected during three longitudinal profiles along the estuarine salinity and turbidity gradients on-board the R/V *Thalia* (IFREMER) in March 2014 (MGTS I, n = 26), March 2015 (MGTS II, n = 23) and October 2015 (MGTS III, n = 26) from Bordeaux to the estuary mouth (Fig. 1) under different discharge conditions: intermediate (Q = 1203 m^3 s^{-1}), high (Q = 3450 m^3 s^{-1}) and low (Q = 260 m^3 s^{-1}), respectively. Water was sampled using Niskin bottles at 1 m depth, immediately filtered onsite through 0.2 μm Minisart® cellulose acetate filters into acid-washed polypropylene (PP) bottles, acidified with HNO_3 (2% J.T. Baker Ultrapure, 14 M) and stored at 4 °C in the dark until analysis. Suspended particle samples were collected into 40 l acid-washed polyethylene (PE) drums with a PP peristaltic pump and PP tubing at 1 m depth followed by on-board centrifugation (Westfalia; 12,000 g; Lapaquellerie et al., 1996), dried (50 °C in a drying oven), grinded and homogenized (agate mortar) and stored at room temperature in the dark until analysis.

A fourth sampling campaign was carried out on board the R/V *Planula IV* (CNRS/INSU) in April 2015 in the Arcachon Bay (Comprian Station, Fig. 1). Water samples were collected at 2.5 m depth with