Science of the Total Environment 435–436 (2012) 345–350

Contents lists available at SciVerse ScienceDirect

Science of the Total Environment

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

New insight into photo-bromination processes in saline surface waters: The case of salicylic acid

Fatima Tamtam, Serge Chiron *

UMR HydroSciences 5569, Montpellier University, 15 Avenue Ch. Flahault, 34093 Montpellier cedex 5, France

HIGHLIGHTS

- ► Brominated derivatives of salicylic acid were detected in a brackish lagoon.
- ► A photochemical pathway was hypothesized to account for bromination of salicylic acid.
- ► Radical bromine species are partly responsible for the bromination process.
- ► Hypobromous acid might be also involved through photo-generation of peroxynitric acid.
- ► Bromination would mainly occur in saline waters impacted by wastewater discharges.

ARTICLE INFO

Article history:
Received 7 May 2012
Received in revised form 5 July 2012
Accepted 5 July 2012
Available online 3 August 2012

Keywords:
Salicylic acid
Bromination
Photolysis
Saline water
Peroxynitrite

ABSTRACT

It was shown, through a combination of field and laboratory observations, that salicylic acid can undergo photo-bromination reactions in sunlit saline surface waters. Laboratory-scale experiments revealed that the photochemical yields of 5-bromosalicylic acid and 3,5-dibromosalicylic acid from salicylic acid were always low (in the 4% range at most). However, this might be of concern since these compounds are potential inhibitors of the 20α-hydroxysteroid dehydrogenase enzyme, with potential implications in endocrine disruption processes. At least two mechanisms were involved simultaneously to account for the photo-generation of brominated substances. The first one might involve the formation of reactive brominated radical species ($Br•$, $Br_2•^-$) through hydroxyl radical mediated oxidation of bromide ions. These ions reacted more selectively than hydroxyl radicals with electron-rich organic pollutants such as salicylic acid. The second one might involve the formation of hypobromous acid, through a two electron oxidation of bromine ions by peroxynitrite. This reaction was catalyzed by nitrite, since these ions play a crucial role in the formation of nitric oxide upon photolysis. This nitric oxide further reacts with superoxide radical anions to yield peroxynitrite and by ammonium through the formation of N-bromoamines, probably due to the ability of N-bromoamines to promote the aromatic bromination of phenolic compounds. Field measurements revealed the presence of salicylic acid together with 5-bromosalicylic and 3,5-dibromosalicylic acid in a brackish coastal lagoon, thus confirming the environmental significance of the proposed photochemically induced bromination pathways.

1. Introduction

Emergent organic contaminants (EOCs) such as pharmaceuticals have been reported in coastal marine waters and brackish lagoons at levels in the ng/L range (Munaron et al., 2011; Magnér et al., 2010). Their fate is probably driven by microbially mediated degradation and photodegradation processes (Benotti and Brownawell, 2009). However, in saline waters, one transformation pathway of concern might be halogenation, since organohalogenated compounds have demonstrated a complex diversity of biologic effects. For instance, brominated and chlorinated bisphenol A analogs have recently demonstrated their ability to activate peroxysome proliferator-activated receptors (PPARs), while their estrogenic potential decreased with respect to bisphenol A (Riu et al., 2011). Bromine ions (Br^-) are potentially of more substantial concern than chloride ions (Cl^-) because, for instance, brominated disinfection by-products (DBPs) are generally more genotoxic and carcinogenic than chlorinated DBPs (Kogevinas et al., 2010). Reports on the photochemical production of organobrominated compounds in saline waters are scarce. Upon simulated solar light irradiation of coastal seawater, 4-bromophenol accounted for about 2% of the total degraded phenol (Calza et al., 2008). Bromophenols accounted for 93–96% of the total halogenated phenols, indicating that bromination reactions prevailed over chlorination reactions, probably due to the higher reactivity of

---

* Corresponding author. Tel.: +33 4 11 75 94 12; fax: +33 4 11 75 94 61.
E-mail address: serge.chiron@msem.univ-montp2.fr (S. Chiron).

0048-9697/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
doi:10.1016/j.scitotenv.2012.07.015

Br^- over Cl^- against oxidation. Bisphenol A was also transformed into 3-chlorobisphenol A and 3,3′-dichlorobisphenol A, but in this latter case brominated derivatives were unfortunately not investigated (Liu et al., 2009). Little is known on the mechanisms involved in covalent incorporation of halogen atoms (Br^- and Cl^-) in organic molecules during photochemical processes. Colored dissolved organic matter has shown some capacity to enhance the photochemical production of methyl chloride (Moore, 2008). Halogenation processes in seawater have often been justified by the formation of reactive halogenated species ($RHS = X\bullet$, $X_2\bullet^-$) through hydroxyl radical mediated oxidation of bromide ions, and through photolysis of iron complexes such as Fe(III) fulvic acid complexes (Liu et al., 2009) that reacted more selectively than hydroxyl radicals with electron-rich organic pollutants such as phenols. Despite occurring at a 675-fold lower concentration than Cl^-, Br^- is the most important scavenger of hydroxyl radicals (HO•) in seawater (Mopper and Zhou, 1990), mainly producing bromine radicals (Br•) since the chlorine radical can be formed by hydroxyl radicals only in a strong acidic solution (Vione et al., 2005). The reaction goes through the intermediate $BrOH\bullet^-$ complex and the following combination with bromine to form dibromine radical anions ($Br_2\bullet^-$). If available in excess, chloride ions can compete to a certain extent with bromide to form $BrCl\bullet^-$, which is also a brominating agent (Grebel et al., 2010). Consequently, photochemical processes in saline waters should mostly yield brominated organic compounds, but with many uncertainties. The present work is an attempt to gain new insight into photobromination mechanisms in saline waters and to assess their environmental significance by carrying out monitoring studies. Salicylic acid (SA) was thus used as a probe compound. SA was selected because: 1) It is probably one of the most frequently detected organic micropollutants in environmental waters (Vulliet and Cren-Olivé, 2011; Lapworth et al., 2012), SA mainly originating from the human metabolization of acetyl salicylic acid (aspirin). 2) Dihalogenated SA derivatives are known to be potent inhibitors of the 20α-hydroxysteroid dehydrogenase (DHS) enzyme (El-Kabbani et al., 2011). DHS plays a key role in the metabolism of progesterone and other steroid hormones, with potential implications in endocrine disruption processes (Thibaut and Porte, 2004) and 3) many potential transformation intermediates of SA are commercially available as standards. To our knowledge, this is the first attempt to investigate the mechanisms of photobromination of SA in saline waters and to validate their occurrence through monitoring studies.

2. Experimental section

2.1. Chemicals

Acetaminophen (APAP > 99%), 2,5-dihydroxybenzoic acid (5-OH-SA > 98%), *p*-benzoquinone (BQ > 98%), salicylic acid (SA > 99%), salicylic acid-d_6 (SA-d_6 > 98%), 5-bromosalicylic acid (5-Br-SA > 90%), 5-nitrosalicylic acid (5-NO_2-SA > 98%), 3,5-dibromosalicylic acid (3,5-Br_2-SA > 97%), formic acid (analytical grade), $NaNO_2$ (> 98%), KCl (> 98%), $NaH_2PO_4 \times H_2O$ (> 98%), $Na_2HPO_4 \times 2\ H_2O$ (99.5%), KOH (99%), HCl (37%), $NaHCO_3$ (> 99.5%), H_2O_2 (30%, v/v), isoamyl nitrite stabilized with 2% sodium carbonate (> 97%), sodium bromide for trace analysis (> 99.9%) and ammonium bromide for trace analysis (> 99.9%) were all purchased from Sigma-Aldrich (Saint Quentin Fallavier, France) and were used as received. Bis(4-carboxybenzyl) hyponitrite (SOTS-1) was obtained from Cayman Chemicals (Ann Arbor, USA). 500 μg aliquots of SOTS-1 was used as received and stored at −80 °C. Immediately prior to beginning any experiments, 500 μg SOTS-1 aliquots were dissolved in 200 μL DMSO (Fluka, puriss p.a. > 99.9%) before further dilution in artificial seawater. The typical final concentration for SOTS-1 was 10 μM. Acetonitrile (LC grade) was purchased from Merck (Darmstadt, Germany). For LC mobile phases and standard dilution, deionized water was further purified with a Milli-Q water purification system (Millipore, Bedford, USA).

2.2. Irradiation procedure

The experiments were conducted in triplicate to ensure the consistency of the results and each kinetic point represented an average of three experiments.

2.2.1. Simulating solar light

The irradiation experiments were carried out in Pyrex glass cells, containing 100 mL of sample. Illumination was performed using a 1500 W Xenon lamp (Suntest, CO.FO.MEGRA, Milan, Italy) equipped with a 340 nm cut-off filter simulating AM1 solar light. The temperature reached during irradiation was 38 °C. SA at 0.1 μM level was spiked into brackish water samples which had been collected at the Thau lagoon (southern France) with a pH of 8.1 ± 0.1 and contained on average 320 mM NaCl, 0.5 mM NaBr, 2.3 mM carbonates, 52 μM nitrate, 28 μM nitrite, 35 μM ammonium and a total organic carbon (TOC) content of 5.4 mg C/L. Due to the low levels of nitrite and nitrate ions, both ions were determined by ion chromatography equilibrated with 5 mM cetyltrimethylammonium chloride aqueous solution allowing for detection limits (S/N = 3) with UV detection at 225 nm of 1.0 and 1.6 μg/L for NO_2^- and NO_3^-, respectively (Ito et al., 2005). The ammonium content was determined by the indophenol-blue method (Aminot et al., 1997). TOC was measured using a Shimadzu-5050A TOC analyzer. One experiment was sacrificed at each sampling time and treated like the WWTP effluent samples (see below).

2.2.2. UV light

SA (100 μM) was added to solutions containing 0.8 mM NaBr, 2.3 mM carbonates and 540 mM NaCl. This kind of solution is hereafter referred to as artificial seawater. After adding 1 mM H_2O_2, they were irradiated with UV light originating from a 200 W high pressure mercury lamp at 37 °C. The UV light intensity was 173 mW/cm^2 at 254 nm. Reactions were quenched with methanol for LC/UV and LC/MS analysis.

2.3. Peroxynitrite assays

Peroxynitrite anions ($ONOO^-$) were prepared from isoamylnitrite in the presence of H_2O_2 and quantified spectrophotometrically ($\varepsilon_{302} = 1670 \pm 50\ M^{-1}\ cm^{-1}$), as previously described (Uppu and Pryor, 1996). Excess H_2O_2 was removed by treatment with MnO_2. In spite of this, the peroxynitrite preparation could contain H_2O_2 residues. To avoid rapid decomposition of $ONOO^-$, stock solutions of peroxynitrite were prepared in KOH 0.1 M (final concentration of 1–10 μM). Peroxynitrite was allowed to react with 100 μM of SA in 10 mL of 0.1 M phosphate buffer, pH 7.0–7.5, that also contained 0.8 mM bromide ions. The reactions were performed by adding aliquots (100–150 μL) of stock peroxynitrite solution to the SA solutions with vigorous stirring for a few seconds at room temperature. Solutions were filtered before direct analysis by LC/UV and LC/MS.

2.4. Field sampling

24 h composite WWTP effluents were collected at the WWTP outlet at the city of Sète (see Fig. 1 in the Supplementary material). Samples were kept in amber glass bottles on ice until arrival at the laboratory, where they were refrigerated at 4 °C. After filtration through 0.45 μm cellulose membrane filters and adjustment of the pH to 3 with HCl, triplicate samples of 250 mL WWTP effluents were extracted on a SPE cartridge (OASIS HLB, 200 mg from waters). Cartridges were conditioned with 6 mL methanol followed by 6 mL Milli-Q water acidified at pH 3 before sample percolation. Analytes were eluted with 2 × 5 mL methanol. The eluate was evaporated under a gentle nitrogen stream and reconstituted with 0.5 mL water/methanol (50/50, v/v). Passive Organic Contaminant Integrative Samplers (POCIS) were deployed within a steel canister inside the Thau