



Seasonal variation and mixing behaviour of glutathione, thioacetamide and fulvic acids in a temperate macrotidal estuary (Aulne, NW France)



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ABSTRACT

Fulvic acids and two dissolved reduced sulphur substances (RSS) were analysed for one year along the whole salinity gradient in the Aulne estuary (north-western France) using differential pulse cathodic stripping voltammetry. Concentrations of glutathione-like (GSH-like), thioacetamide-like (TA-like) and fulvic acid-like (FA-like) compounds ranged from 0.2 to 38 nmol L⁻¹, from 0.02 to 6.6 μmol L⁻¹ and from 0.1 to 4 mgC L⁻¹, respectively. Our results indicated primarily allochthonous-continental sources for all three compounds. The behaviour of GSH-like compounds along the salinity gradient was globally conservative, with minor losses (<25%), possibly limited due to metal complexation. TA-like compounds generally displayed non-conservative behaviour with important removals. In terms of the TA-like budget, losses were counterbalanced by exceptional inputs occurring in the flood period (February). FA-like compounds were intensely degraded (~50%) in the last section of the river and then behaved conservatively in the estuary. The annual flux of FA-like compounds to coastal waters was 2800 ± 600 tC. This flux was mainly (74%) delivered during the high discharge period, in accordance with its known pedogenic origin.

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1. Introduction

A better understanding of the fate of dissolved organic matter (DOM) during its estuarine transport requires the investigation of various constituents of the DOM pool (Hedges et al., 1997). For example, the conservative behaviour of dissolved organic carbon (DOC), one of the most common parameters used to quantify bulk natural organic matter (NOM) (Filella, 2009), may hide the simultaneous release and use of different compounds. Consequently, its study may mask other processes in estuaries (Cauwet, 2002). Among the major groups of compounds representative of DOM, reduced sulphur substances (RSS) and humic substances have stimulated interest. RSS are ubiquitous at the millimolar level in intracellular media, participate in a wide range of biochemical reactions and quickly undergo oxidation processes in surface waters (Mopper and Kieber, 2002; Jacob et al., 2003). In contrast, humic substances mainly derive from the decay of terrestrial lignin-containing plants (Dittmar and Kattner, 2003). They are generally considered recalcitrant in aquatic systems but can at least partially be decomposed by microorganisms (Rocker et al., 2012) and are photoreactive (e.g. Benner and Kaiser, 2011).

RSS, particularly thiol, contain one of the most reactive functional groups found in eukaryote cells (Gruhlke and Slusarenko, 2012). One thiol, glutathione (GSH), a tripeptide, is the most dominant and abundant low molecular weight cellular thiol in animals, plants and bacteria (Jacob et al., 2003). GSH is believed to play an important role in protecting cells against oxidative stress and also in decreasing metal toxicity (Noctor and Foyer, 1998; Jacob et al., 2003). It is also one of the most abundant RSS found in aquatic environments (Tang et al., 2000). GSH, is released by marine phytoplankton in surface seawater during the life cycle (Dupont et al., 2004; Hu et al., 2006) or in response to metal stress (Ahner et al., 2002; Tang et al., 2004; Kawakami et al., 2006). In anoxic porewaters, GSH production may result from the bacterial degradation of sulphur-containing amino acids (Zhang et al., 2004). Other specific RSS, such as thioacetamide (TA), cysteine or thiourea, may be also detected in surface waters but their origin has not yet been demonstrated (Laglera and Tovar-Sanchez, 2012; Superville et al., 2013; Marie et al., 2015). Their low micromolar or nanomolar concentrations and low stability in aquatic systems make them difficult to analyse, thereby limiting environmental surveys. Studies on the behaviour of RSS during estuarine mixing are scarce, with most of them involving GSH, and are usually limited in scale-time (one or two sampling campaigns), preventing the analysis of important factors varying seasonally (e.g. nature of OM being

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exported from watershed, phytoplankton or bacterial production). A few authors have demonstrated that GSH behaves conservatively (Le Gall and van den Berg, 1993; Laglera and van den Berg, 2003; Han et al., 2006). This stability of GSH has been attributed to strong metal complexation (Tang et al., 2004; Moingt et al., 2010). For example, metals such as Cu have a high affinity for thiols (Leal and van den Berg, 1998; Dryden et al., 2007). In other studies, various non-conservative behaviours have been observed. Laglera and van den Berg (2006) showed that thiol concentrations decrease in surface water by 30–50% after one day of exposure to sunlight with a half-life of 3 h. In contrast, inputs at mid-estuary are observed upon GSH release from various algal species (Tang et al., 2000).

Humic substances is an operationally defined fraction of DOM (Thurman and Malcolm, 1981) which can be further separated into three components according to solubility: humic acids (HA), fulvic acids (FA) and humin (Stevenson, 1994). They are a complex mixture of high molecular weight molecules originating from the breakdown of terrestrial organic matter and represent the major component of DOM in rivers and estuaries (>80% of DOC) (Pettersson et al., 1997; Waeles et al., 2013). Similar to RSS, the behaviour of humic substances during transport to the marine environment is still unclear. Some studies report the preservation of FA, the predominant humic substances fraction in freshwater, under estuarine mixing (Ertel et al., 1986; Nouredin and Courtot, 1989; Otero et al., 2003; McKenna, 2004; Tremblay and Gagné, 2009; Waeles et al., 2013). In contrast, other studies have shown that HA are removed at the early stage of estuarine mixing by flocculation and precipitation (Sholkovitz et al., 1978; Fox, 1983; Ertel et al., 1986; Asmala et al., 2014b) and that humic substances are subject to important bacterial degradation when reaching coastal marine conditions (Kisand et al., 2013).

In this study, we examined the seasonal variation and mixing behaviour of GSH-like, TA-like and FA-like compounds across the salinity gradient of the Aulne estuary (NW France). These groups of compounds were analysed at a mercury drop electrode (pH 1.95) using a recently-developed differential pulse cathodic stripping method (DP-CSV; Pernet-Coudrier et al., 2013). Twelve stations were sampled monthly during one hydrological year (December 2013 to December 2014) to cover the relatively high variations of this dynamic system. The first objective was to understand the seasonal variations of these organic compounds that might be influenced by the nature of OM being exported from the watershed or by other important factors controlling their synthesis or their degradation in waters. The other goals were to examine their behaviour during estuarine mixing and to estimate their fluxes towards the coastal ocean.

2. Materials and methods

2.1. Study area

The Aulne river (Brittany, France) has a drainage area of 1900 km², is 144 km long and is the main river discharging into the Bay of Brest (average of 29 m³ s⁻¹ over the 2010–2015 period) (Fig. 1). Anthropogenic activities in the Aulne watershed are mainly agricultural, i.e. vegetable cultivation and animal farming. Soil occupancy is mainly in arable and permanently cultivated areas (40%) and in heterogeneous agricultural areas (33%). The remaining non-urbanised areas comprise meadows (8%), moors and peat bogs (5%), and forests (11%). Change in the Aulne water discharge is constrained by a temperate oceanic climate. Rain falls all year round (annual rainfall usually around 1500 mm), with a distinct maximum during winter, mainly from the regular procession of weather fronts that move east across the Atlantic. As a result, ~60%

of the annual flow generally occurs in the December–March period. The Aulne estuary is characterised by a macrotidal regime, with a tidal range that fluctuates between 1.2 and 7.3 m. The residence time of water within the estuary is firstly controlled by the river flow and is also dependant on the tidal range (Bassoullet, 1979). For our survey, the residence time of water was estimated to vary between ~5 days (February 2014) to 20–30 days (June–September period). No dredging was performed in the estuary in 2014 (SMA-TAH, Finistère).

2.2. Sampling

Estuarine waters were collected monthly from December 2013 to December 2014. To cover the whole salinity gradient, sampling stations were selected according to their salinity ($S_{\text{surface}} \approx 0, 3, 6, 9, 12, 15, 18, 21, 24, 28, 30$ and 34). In January and February, very high discharge hindered sampling at the high salinity (30–34) stations. In order to limit the tidal effect, each set of samples was always collected during neap tides (Table 1). Sampling was started from the salinity front ($S = 0$) at high tide. The inner part of the system of ~15 km long ($S < 15$) was sampled within the first hour over which the tidal flow was low (tidal flow under 20 cm s⁻¹, Bassoullet, 1979). Then sampling of the outer wide-open part of the system and the bay of Brest (~35 km long) was performed until typical seawater ($S = 34$) ending at high tide + ~3 h. Samples were collected by hand at about 0.5 m depth in prebaked 500 mL (450 °C, 4 h) glass bottles (Schott®) which were stored cool in dark boxes until filtration. Long gloves were worn during sampling (92 cm, Polysem®). Water samples were also collected close to the bottom at three stations ($S_{\text{surface}} \approx 6, 9, 15$) with a Niskin bottle (except in March). Salinity was measured *in situ* using a multi-element probe (Hanna®, HI 9828), calibrated daily with KCl solution (Hanna®, 1413 μS cm⁻¹). In addition to the estuary samples, river samples were collected weekly at Pont Coblant (7.5 km upstream from Châteaulin, Fig. 1), where the tide has no influence.

2.3. Sample treatment and reagents

For all estuarine water samples, between 100 and 500 mL was filtered in the laboratory within 3 h of collection on 0.7 μm GF/F membranes (Ø25 mm, Whatman®) which were immediately stored at -20 °C until Chlorophyll-*a* (Chl_a) and phaeopigments (phaeo) measurements. Filtered water was acidified at pH 2 (with 3% HCl, Suprapur®, Merck), poured in prebaked (450 °C, 4 h) brown glass bottles and frozen (-20 °C) until analysis of FA-like, GSH-like and TA-like. Suspended particulate matter (SPM) was collected on 0.45 μm HATF filters (Ø47 mm, Millipore®). Prior to use, all items employed for sampling and filtration were washed with diluted hydrochloric acid (pH 2, HCl Suprapur®, Merck) then rinsed thoroughly with ultrapure deionised water (>18.2 MΩ; Millipore® Milli-Q Element system). Ultrapure deionised water was used for cleaning and preparation of reagents and working solutions.

2.4. Analyses

Analyses of the various compounds was performed by differential-pulse cathodic stripping voltammetry (DP-CSV) (Pernet-Coudrier et al., 2013) using standard addition of glutathione (GSH), thioacetamide (TA) and fulvic acid (FA) standard solutions. As previously explained by Pernet-Coudrier et al. (2013), analytical targets, which are operationally defined, correspond to glutathione-like, thioacetamide-like and fulvic acid-like compounds that will thus be referred here as GSH-like, TA-like and FA-like. However, it is worth remaining that the FA-like signal corresponds to humic substances which is relative to both FA and HA

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