



# Dynamics and sources of reduced sulfur, humic substances and dissolved organic carbon in a temperate river system affected by agricultural practices



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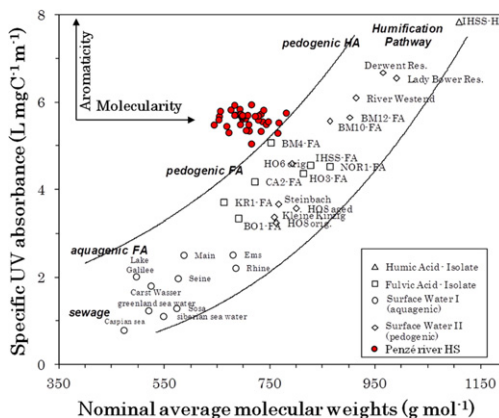
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## HIGHLIGHTS

- Thiols and dissolved organic carbon were measured in an agricultural river over 1 year.
- Humic substances were washed out from the soil mainly during the floods.
- Thioacetamide-like compounds had a clear groundwater source.
- Glutathione had 2 sources linked to primary productivity and bacterial degradation.
- DOC flux was 280 tC/year and HS, TA and GSH account for 60, 13 and 4% of the DOC flux, respectively.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

### Article history:

Received 19 June 2015

Received in revised form 17 July 2015

Accepted 17 July 2015

Available online 12 August 2015

Editor: D. Barcelo

### Keywords:

Annual flux

Dissolved organic matter

Fulvic acid

Glutathione

Origin

Thioacetamide

Thiols

## ABSTRACT

Although reduced organic sulfur substances (RSS) as well as humic substances (HS) are widely suspected to play a role in, for example, metal speciation or used as a model of dissolved organic carbon (DOC) in laboratory studies, reports of their quantification in natural waters are scarce. We have examined the dynamics and sources of reduced sulfur, HS and DOC over an annual cycle in a river system affected by agricultural practices. The new differential pulse cathodic stripping voltammetry was successfully applied to measure glutathione-like compounds (GSHs), thioacetamide-like compounds (TAs) and the liquid chromatography coupled to organic detector to analyze HS and DOC at high frequency in the Penzé River (NW France). The streamflow-concentration patterns, principal components analysis and flux analysis allowed discrimination of the source of each organic compound type. Surprisingly, the two RSS and HS detected in all samples, displayed different behavior. As previously shown, manuring practice is the main source of DOC and HS in this watershed where agricultural activity is predominant. The HS were then transferred to the river systems via runoff, particularly during the spring and autumn floods, which are responsible of >60% of the annual flux. TAs had a clear groundwater source and may be formed underground, whereas GSHs displayed two sources: one aquagenic in spring and summer probably linked to the primary productivity and a second, which may be related to bacterial degradation. High sampling frequency allowed a more accurate

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assessment of the flux values which were  $280 \text{ tC y}^{-1}$  for DOC representing  $20 \text{ kgC ha}^{-1} \text{ y}^{-1}$ . HS, TAs and GSHs fluxes represented 60, 13, and 4% of the total annual DOC export, respectively.

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## 1. Introduction

Dissolved organic matter (DOM) is formed from the decay of intact or remnant and transformed compounds released from living and decaying biota. Because it participates in many biogeochemical processes in the environment, i.e. photochemical reactions, metal complexation, microbial growth, and nutrient and contaminant transport, DOM is an important component of marine and terrigenous aquatic ecosystems. Therefore, determining its composition and reactivity is essential for understanding environmental processes, for example metal complexation. Moreover, the riverine export of DOM through estuaries has a major impact on the biogeochemical cycles in the coastal ocean (Canuel et al., 2012; Hansell and Carlson, 2002; Volkman, 2006). Despite its importance, the composition and fate of riverine DOM have been poorly determined and remain one of the major concerns in contemporary biogeochemistry (Bianchi, 2011).

A significant proportion of riverine DOM is composed of more stable compounds produced either in the soil or in the water body. Because of their resistance to degradation, these compounds are sometimes called refractory organic matter (ROM), but they are most often referred to as humic acids (HA), fulvic acids (FA) or humic substances (HS). As mentioned recently (Filella, 2014), although HS are the most widely used type of DOM in laboratory studies, attempts to quantify them in natural waters are scarce. The only quantification method that will theoretically allow measurement of 'true' HA and FA concentrations should be based on exactly the same fractionation procedure used in defining them. However this requires large volumes of water, and is tedious and time-consuming, so is rarely used. Due to an update of an old electroanalytical method (Quentel et al., 1986), a few studies of the HS behavior in the aquatic environment have appeared (Chanudet and Filella, 2007; Filella et al., 2013; Waeles et al., 2013).

Besides, reduced sulfur substances (RSS), particularly thiols have aroused interest mainly because they are important complexing ligands for metals and therefore significantly control the speciation of many trace elements in natural waters by competing with other potential binders such as HS (Buffle, 1988). Thiols are ubiquitous at the mmol level in intracellular media and participate in a wide range of biochemical reactions due to their detoxifying effect as metal ligands and reactive oxygen species scavengers (Jacob et al., 2003). It was long assumed that the concentration of thiols would be quite low or even below detection in oxic waters as these compounds are readily oxidized (Abedinzadeh et al., 1989; Winterbourn and Metodiewa, 1999), easily metabolized by bacteria (Visscher and Taylor, 1993) and/or quickly photo-oxidized (Laglera and van den Berg, 2006; Moingt et al., 2010). It has been demonstrated, however, that thiols like glutathione may be stabilized via metal complexation or even DOM conjugation (Moingt et al., 2010; Tang et al., 2004). Most studies reporting on thiols in aquatic systems have been conducted on marine, estuarine and coastal environments, and have generally found a correlation between some thiols and indicators of phytoplankton abundance, particularly chlorophyll (Chl-*a*) concentration (Al-Farawati and van den Berg, 2001; Dupont et al., 2006; Laglera and van den Berg, 2003; Le Gall and van den Berg, 1993; Tang et al., 2000, 2004). Only three studies have reported thiols in freshwater: Connecticut lakes (Hu et al., 2006), the St Lawrence system (Moingt et al., 2010) and one focusing on sediment porewater in a wetland area (Zhang et al., 2004).

Determination of the individual components of RSS mixtures in the range  $\text{pmol L}^{-1}$  to  $\mu\text{mol L}^{-1}$  may be performed using high performance liquid chromatography (HPLC) after derivatization (Dupont et al., 2006; Tang et al., 2003, 2004). However, uncertainty about the recovery rates

and the common presence of unidentified thiol peaks may pose some concern about the ability of HPLC to determine the overall concentration of RSS. The huge affinity of reduced sulfur for mercury facilitates the analysis of RSS using cathodic stripping voltammetry (CSV) with mercury electrodes. However, CSV is severely limited by coalescence at neutral pH, i.e. thiol peaks merge together at environmental pH. Recent electroanalytical improvements by way of cathodic pseudopolarography (Laglera et al., 2014; Laglera and Tovar-Sanchez, 2012), enabled the characterization and quantification of individual components of RSS mixtures at neutral pH. The duration of the analysis (several h per sample) is, however, too restrictive for environmental applications. Nevertheless it has been shown recently that acidification of the samples to pH 1.95 and addition of molybdenum (VI) allow the rapid and direct simultaneous identification and quantification of glutathione (GSH), thioacetamide (TA) and HS using differential pulse CSV (DP-CSV) (Pernet-Coudrier et al., 2013).

In this study, we investigated the behavior of DOC, HS and RSS in the Penzé River (NW France) using DP-CSV and liquid chromatography coupled to an organic carbon detector. Despite its low discharge regime, this river can be regarded as a typical temperate system affected by agricultural practices (Waeles et al., 2005, 2013). Moreover, studies on such small watersheds over a wide range of hydrologic conditions also allow understanding relative short-term components of carbon cycling (Dalzell et al., 2005). Therefore, the Penzé River had been sampled at high frequency over a 1 year period (45 sampling campaigns in 2012) in order to take into account the potential strong variability. To our knowledge, such an approach has not been undertaken before. Our objectives were to (i) determine the annual dynamics of DOC, RSS and HS in this kind of temperate river system affected by agricultural activity, (ii) to examine the sources of these compounds and (iii) to assess their flux towards the coastal area.

## 2. Material and methods

### 2.1. Study area

The Penzé River (N Brittany, France) has a drainage area of  $141 \text{ km}^2$  and is 28 km long, with an estuary of 10 km (Fig. 1). This river system collects the water from a poorly industrialized catchment but where extensive agricultural activity has been developed for decades. Soil occupancy is mainly agricultural with arable and permanently cultivated areas representing 36% and heterogeneous agricultural areas accounting for 33%. Meadows (7%), moor and peat bogs (3%) and forests (0.7%) are the remaining non urbanized areas. Agricultural activity consists mainly of farming and vegetable cultivation. The water discharge at the village of Penzé usually fluctuates in the range  $0.6\text{--}14.5 \text{ m}^3 \text{ s}^{-1}$  with an average of  $2.8 \text{ m}^3 \text{ s}^{-1}$  during the 1967–2013 period. Evolution of the water discharge in the system is constrained by a temperate oceanic climate and, as a result, 60% of the annual flow generally occurs in the December–March period.

### 2.2. Sampling and in situ measurements

The river was sampled during one hydrological year from 05/01/2012 to 09/01/2013 with an 8 day frequency at Prat Guen ( $3^{\circ}54'42.5'' \text{ W}$ – $48^{\circ}31'18.8'' \text{ N}$ ) 1 km from the village of Saint Thégonnec, outside the turbid area and upstream of the salty zone of the estuary (Fig. 1). Samples were collected in Teflon separatory funnels by hand from ca. 0.2 m below the surface, with the arm fully covered with a plastic glove (92 cm, Polysem®). River water samples were filtered on site immediately after sampling. Chlorophyll-*a* (Chl-*a*) was collected on  $0.7 \mu\text{m}$

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