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Free phenolic compounds in waters of the Ross Sea

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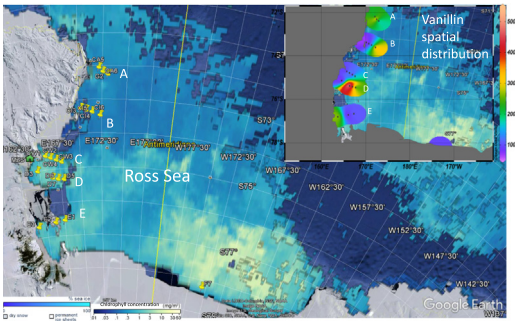
HIGHLIGHTS

- PC in particulate and in dissolved fractions of Ross Sea waters were determined.
- PC were mainly VA, VAH, VAC and PA; Highest concentrations in dissolved phase.
- PC in Antarctic seawater explain the PC presence in Antarctic atmosphere.
- High PC and Fluo, Chl *a* and Pheo were concomitant suggesting an algal origin.
- Results indicate that PC can have other source than biomass burning in Antarctica.

GRAPHICAL ABSTRACT



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ABSTRACT

The presence of free phenolic compounds (PC) in Antarctic sea water has been investigated to explain their source and particle size distribution in the atmospheric aerosols, as determined in our previous research. The sea water samples were filtered to distinguish the PC concentrations in the particulate and dissolved fractions. Two sample preparation procedures were developed to quantify nine PC in both fractions. The highest concentrations were found in the dissolved fraction of Ross Sea water, with vanillin, vanillic acid, acetovanillone and *p*-coumaric acid being the most abundant PC. Dissolved PC were mainly found in the upper part of water column. This facilitated the sea water-air exchange by bubble busting processes. In the aerosol, they were mainly found in the fine fraction, where these compounds have a higher degree of oxidation than PC detected in seawater, suggesting that they were newly emitted and they have been not yet oxidized. These results supported our previous hypothesis that PC were locally emitted into the atmosphere from the Ross Sea.

Three different possible sources of PC are hypothesized for Antarctic sea waters: 1) from the intrusion of Modified Circumpolar Deep Water that may transport oceanic lignin; 2) from phytoplankton biomass that may be a source of PC in Antarctic waters since diatoms produce exudates that contain vanillic acid, *p*-coumaric acid and syringic acid; 3) from the melting of glaciers and sea ice: glaciers contain lignin that can be degraded, while in the sea ice there are diatoms that may release PC.

Statistical analysis and the low value of vanillic acid/vanillin ratio indicated that the most plausible source for PC in the dissolved fraction was the senescence of phytoplankton. As a contrast, particulate PC with higher vanillic acid/vanillin ratios were ascribed to degraded lignin or the sorption of diagenically oxidized material on particles.

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1. Introduction

Phenolic compounds (PC) are compounds of plant origin because they are the building blocks of lignin. Lignin is a biopolymer that makes up one third of dry wood biomass (Jex et al., 2014; Li et al., 2012), and it is ubiquitous in the environment. Lignin contains three main phenolic groups: the vanillyl, the syringyl and the cinnamyl moieties and their relative abundances can be used to distinguish between types of plants. While softwoods contain mainly vanillyl moieties, hardwoods prevalently include syringyl groups, and grasses are rich in cinnamyl substrates (Oros et al., 2006; Oros and Simoneit, 2001a; Oros and Simoneit, 2001b). Since lignin is relatively resistant to microbial degradation in comparison to other plant components, it is widely used as an indicator of organic matter in riverine, lacustrine and marine waters (Li et al., 2012; Opsahl and Benner, 1997), as well as an indicator for specific vascular plants (Jex et al., 2014; Li et al., 2012; Opsahl and Benner, 1997). Lignin is also an important component of organic matter in soil, peats and sediments (Jex et al., 2014). As the chemical composition of lignin is indicative of wood type, it is often used during paleoenvironmental research on soils and sediments (Jex et al., 2014). Lignin can be biologically and photochemically degraded (Benner and Kaiser, 2011; Jex et al., 2014). Compounds produced from lignin degradation are found in soils (Thevenot et al., 2010), in rivers and the sea.

Free PC are molecular tracers also produced by lignin pyrolysis (Simoneit et al., 1999). When they are injected into the atmosphere during biomass burning, their proportions are indicative of the type of wood combusted (Zangrando et al., 2016a). Some free PC, such as vanillic acid, have also been proposed as additional biomass burning tracers in ice core paleorecords (Giorio et al., 2018; Grieman et al., 2015; McConnell et al., 2007; Wolff et al., 2012). However, free PC have been rarely determined in river or sea water (Edelkraut, 1996; Keil et al., 2011).

Recently, a study on Antarctic aerosols collected at a coastal site and on the plateau highlighted a different particle-size distribution and different seasonal trends between levoglucosan, an unambiguous biomass burning tracer, and free PC (Zangrando et al., 2016b; Zangrando et al., 2013).

The aim of this paper is to identify plausible sources of PC in the Antarctic environment and to explain their particle size distribution in atmospheric aerosol and their relative abundances in comparison to levoglucosan. Due to the lack of vegetation in Antarctica, and the fact that ice-free areas account for less than 2% of the surface area, the most probably local source should be the ocean. In this work have been developed two HPLC-MS/MS analytical methods to determine vanillic acid (VA), vanillin (VAH), syringic acid (SyA), syringaldehyde (SyAH), homovanillic acid (HA), isovanillic acid (IVA), *p*-coumaric acid (PA), acetovanillone (VAC) and acetosyringone (SyAC) in the dissolved and particulate phases of sea waters. These methods were applied to Ross Sea water samples collected during the 2011–2012 expedition of the Italian National Research Programme in Antarctica. To the best of our knowledge, this is the first study on free PC concentrations and their distribution in Antarctic sea waters.

The main goal of this paper was to compare PC concentrations found in sea water samples with those previously reported in atmospheric aerosols samples (Zangrando et al., 2016b).

2. Experimental

2.1. Materials

The list of materials used is reported in the Supporting material section: Materials.

2.2. Water sampling in the Ross Sea

The twenty-seven water samples were collected in the Ross Sea during the R/V Italica cruise from January 26 to February 8, 2012. The sampling area was divided as described in the sampling plan (Fig. 1 and sampling details in Table 1) into five transects near Cape Adare (CA) (transect A), Coulman Island (CL) (B), Cape Washington (CW) (C), and in three polynya areas: Terra Nova Bay (TNB) (D), Mc Murdo Sound (MMS) (E) and the Ross sea (F).

Sea water samples were collected at the fluorescence profile maximum obtained from CTD fluorescence measurements in the μg L^{-1} range (Chelsea Technologies Group Aqua 3 Chlorophyll a sensor) to collect specific samples at the primary biomass production maximum.

Sampling was performed using a *rosette* of 24 12 L Niskin bottles with a companion SBE9/11 plus CTD probe (Sea Bird Scientific) with sensors for dissolved oxygen, temperature, fluorescence, salinity and conductivity. The sea water samples were immediately filtered onboard using a glass microfiber filter GF/F (porosity 0.7 μm, diameter 47 mm, Whatman, Maidstone, UK), previously cleaned at 400 °C for 4 h, to separate the dissolved and particulate fractions.

At 4 sampling sites (E1, E3, D3 and D7, Fig. 1) three samples that bracketed the fluorescence maximum were collected (above, below and at fluorescence maximum) to define the vertical distribution. The wet filters were enveloped in a double layer of aluminum foil, while the water samples were transferred to polyethylene bottles. Both samples were stored at −20 °C until analysis.

An aliquot of the water samples collected at the fluorescence maxima were buffered with a 4% (v/v) formalin solution for phytoplankton counting.

2.3. Sample processing

2.3.1. Free phenolic compounds in the dissolved fraction

A 500 mL sample of filtered sea water acidified with formic acid (2% v/v, pH = 5) in a volumetric flask was spiked with 250 ng (absolute amount) of $^{13}C_6$ labeled VAH (VAH*) and $^{13}C_1$ labeled VA (VA*). Samples clean-up and pre-concentration was performed using OASIS HLB SPE cartridges (6 cc, 200 mg sorbent per cartridge, Waters). The cartridges were conditioned under vacuum with methanol (5 mL), and equilibrated with formic acid (2% v/v) in water (5 mL). The sample was then loaded onto the cartridge. The sea salt matrix was eliminated by washing the SPE cartridge with 5 mL of ultrapure water before elution. PC were eluted from the cartridge into a 7 mL vial at atmospheric pressure with 5 mL of methanol, however, this solvent strength would cause the immediate elution of the compounds during injection causing peak broadening. To prevent this a 250 μL aliquot of the sample was diluted to a final volume of 1 mL with water to reduce the eluent strength of the solvent in which the samples are dissolved, as reported by Kromidas (2000).

2.3.2. Free phenolic compounds in particulate fraction

The determination of free PC in the particulate fraction was performed after breaking the filter into small pieces and transferring them into a 1.5 mL Eppendorf tube that was previously washed with methanol, then extracting them with 1.5 mL of a 50:50 water-methanol, solution for 30 min. To the samples, 38 ng (absolute amount) of VAH* and VA* were added and the extract was then filtered using a PTFE syringe filter (4 mm, 0.2 μm, Phenomenex, Torrence, CA, USA). A 500 μL of sample in methanol was then diluted with 500 μL of water before analysis, to improve peak shape as described above. Field blanks were obtained analyzing GF/F previously cleaned by heating them at 400 °C for 4 h using the same extraction procedure.

2.4. Instrumental methods

The HPLC/(-)ESI-MS/MS instrumental method used in the present paper was the same reported by Zangrando et al. (2013) with the introduction of the mass spectrometer parameters to simultaneously determine acetovanillone and acetosyringone. Briefly: the chromatographic separation was obtained using a Zorbax Extend C18 (150 mm