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Comparison between DAX-8 and C-18 solid phase extraction of rainwater dissolved organic matter

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ABSTRACT

Rainwater is a very low concentrated matrix and, for dissolved organic matter (DOM) characterization, an efficient extraction procedure is essential. Isolation procedures based on the adsorption onto XAD-8 and C-18 sorbents have been used in the literature for rainwater DOM isolation, but a comparison between these procedures is lacking. In this work, UV–visible and molecular fluorescence spectroscopies highlighted differences between rainwater DOM isolated by DAX-8 (replacement for XAD-8) and by C-18. It was possible to recover higher rainwater DOM percentage by the C-18 based procedure than by the DAX-8 one. Rainwater protein-like compounds were better concentrated by the C-18 procedure than by the DAX-8 one, while humic-like compounds were similarly concentrated by both procedures. Furthermore, rainwater DOM extracted by the C-18 procedure was more representative of the global matrix, while DAX-8 preferentially extracted humic-like compounds.

1. Introduction

Dissolved organic matter (DOM) is defined operationally, almost universal consensus, as the organic matter that passes through a filter of 0.45 μm pore diameter [1,2]. Although there are techniques that can be applied directly to rainwater samples for the characterization of DOM, such as fluorescence spectroscopy, a deeper knowledge of DOM requires a previous extraction from samples. Ultrafiltration or solid-phase extraction, using XAD or C-18 sorbents, are the main ways used to concentrate and isolate DOM from water samples for further analysis [3]. However, there is no single technique that can achieve quantitative isolation of all organic solutes from water [4] and properties of DOM isolated with different techniques may differ markedly [3,5–7]. Besides, some isolation techniques allow for the selective isolation of a certain DOM fraction, which may be advantageous when the aim is obtaining more homogeneous fractions for further characterization.

A vast literature exists on solid phase extraction of organic matter (OM) from matrixes such as soil, freshwater or marine water. Unlike soil and freshwater OM, there is neither a robust protocol for the quantitative isolation of marine DOM nor any commercially available marine reference sample with which to compare extraction efficacy or DOM characteristics of the isolate [8] so the debate on this topic remains. A similar situation has also been already created for water soluble organic matter (WSOM) from aerosols [9], although research on this OM is quite recent, compared with that on marine DOM. Regarding rainwater, the study of the dissolved organic fraction was especially pushed by Willey et al. [10] and most of the references on this matter have been published subsequently. Among these references, even when rainwater is a very low concentrated matrix and, thus, concentration is particularly relevant for the study of DOM, to our best knowledge, DOM extraction has only been referred in four published works [11–14].

Wang et al. [11], in a work not exclusively focussed in rainwater, applied the methodology used for the isolation of aquatic humic substances, which was based on the fractionation of the dissolved organic carbon (DOC) of the water samples into hydrophobic and hydrophilic fractions using Amberlite XAD-8 resin.

Kieber et al. [12] extracted chromophoric dissolved organic matter (CDOM) from rainwater using C-18 cartridges by a method previously described for the isolation of marine DOM [15]. Then, Miller et al. [13], carried out solid phase extraction of CDOM from rainwater by C-18 cartridges, stating that they were employing the extraction technique previously described by Kieber et al. [12]. Both works highlighted that C-18 was chosen because earlier studies had found that, relatively to XAD, C-18 was able to better retain the UV–visible and fluorescence characteristics of isolated chromophoric organic material, which was supported by referring the

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work by Amador et al. [15]. However, Amador et al. [15] is a work on extraction of humic substances (HSs) from seawater and the elution procedure was different from the one used by Kieber et al [12]. Furthermore, the International Humic Substance Society (IHSS) (http://www.ihss.gatech.edu) operationally defined dissolved HSs on the base of adsorption on XAD-8 [16]. Also, seawater and rainwater are very different matrixes. Thus, rigorously, conclusions on HSs from seawater by Amador et al. [15] should not be taken as valid for CDOM from rainwater.

Finally, the procedure used for the isolation and extraction of DOM from rainwater by Santos et al. [14] was adapted from the one used by Duarte and Duarte [17] for isolating WSOM from atmospheric aerosols. Santos et al. [14] highlighted that XAD-8 was able to isolate the most hydrophobic macromolecular rainwater organic solutes.

The present work aims at comparing DAX-8, the available replacement for XAD-8 [18,19], and C-18 procedures for the isolation of rainwater DOM. For this first comparison, UV–visible and molecular fluorescence spectroscopies were used because they can be applied to rainwater samples with low DOC concentrations, without pre-concentration, allowing to follow the DOM isolation process. Moreover, the techniques are rapid and non-destructive, and the molecular fluorescence spectroscopy is a very sensitive technique which detects subtle differences in properties and distribution of fluorophores. Thus, spectra were determined for rainwater and the effluents and eluates from each of the applied isolation procedures. Finally, since research on rainwater DOM is still progressing, this work will be a major contribution for choosing the adequate method of DOM extraction from rainwater.

2. Experimental

2.1. Rainwater sampling and sample preparation

Rainwater was collected at a sampling station (40°38′ N, 8°39′ W) located in the western part of the town of Aveiro, Portugal: one sample was collected in June of 2009 (J09) and two samples were collected in October of 2009 (O09a and O09b). Collection was carried out 70 cm above the ground, through glass funnels (30 cm diameter) into glass bottles (5 L). Sampling containers were left out open in order to collect both wet and dry depositions on a 24 h basis. Prior to use, all glass materials were immersed for 30 min, in a solution of NaOH (0.1 M), then rinsed with distilled water, followed by another immersion for 24 h in a solution of HNO_3 (4 M), and finally rinsed with ultrapure (Milli-Q) water. After collection, samples were transported to the laboratory where they were filtered through hydrophilic PVDF Millipore membrane filters (0.45 μm). In all cases, rainwater was dark stored in glass vials at 4 °C for a maximum of four days, which was verified not to alter the optical properties of samples.

2.2. Fulvic acids solution preparation

For further comparison of the DOM isolation procedures considered in this work, in what concerns their capacity to isolate the humic fraction from rainwater or from other aqueous samples, both procedures were also applied to a known and previously characterized sample of fulvic acids. Fulvic acids (FA) extracted [20] from river Vouga at Carvoeiro, Aveiro, Portugal, were used for this purpose. That sample of fulvic acids has been isolated using the XAD-8 procedure recommended by the IHSS. It is worth to notice that the DAX-8 isolation procedure used in the present work uses a different elution procedure, with methanol/water instead of NaOH 0.1 M. Solutions of 2 ppm of these FA were prepared in ultrapure water and three replicate extractions of DOM were carried out as described below, exactly in the same way as for rainwater.

2.3. DOM extraction

Rainwater samples (500 mL) and FA solutions (500 mL) were subjected to two different procedures for the isolation and extraction of DOM: one based on the use of Supelite™ DAX-8 resin (considered the substitute of XAD-8 since the production of the latter stopped [18]), and another one based on the use of C-18 sorbent (Supelclean envi-18 cartridges, Supelco, 500 mg mass, volume size 6 mL).

The Supelite™ DAX-8 resin is comprised of a poly(methyl methacrylate) resin (pore size = 225 Å; surface area = 160 m^2/g), which is slightly polar, while C-18 sorbent is constituted by alkyl chains of C-18 covalently bonded to a silica substrate (pore size = 60 Å; surface area = 475 m^2/g) being non polar (highly hydrophobic). DAX-8 and C-18 isolation procedures separate DOM into polar and non polar fractions taking into account the molecular size of the solutes and interactions between them and the sorbents.

The isolation procedure based on DAX-8 was adapted from the one described by Santos et al. [14] for the extraction of DOM from rainwater. Fig. 1(a) represents the schematic diagram of the exper-

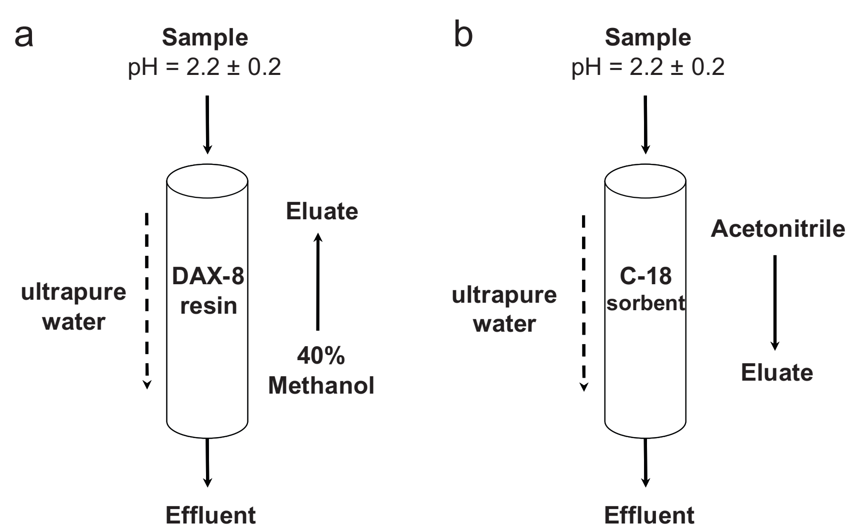

Fig. 1. Schematic diagram of the experimental procedures adopted for DOM isolation.