



Short communication

Evaluation of salinity effect on quantitative analysis of aquatic humic substances using nonionic DAX-8 resin



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HIGHLIGHTS

- Salinity effect on the adsorption behavior of AHS onto the DAX-8 has been examined.
- Salinity will not significantly affect the adsorption behavior of AHS onto the resin.
- Salinity will not hinder comparison of results regardless of solution salinity.

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ABSTRACT

A nonionic macroporous resin, Amberlite[®] XAD-8, or its substitute, Supelite[™] DAX-8, is used when isolating or quantifying aquatic humic substances (AHS). However, the effect of salinity on the adsorption behavior of AHS onto the resin is yet to be confirmed, rendering the possibility of salinity-induced changes in the values of quantified amounts or characteristics of AHS obtained from a salty system. To verify the results of quantification and isolation of AHS using the resin in different salinity systems, the effect of salinity on such quantitative analyses of AHS has been examined. It has been concluded that the salinity effect is in general trivial and will not hinder comparison of results regardless of sample solution salinity.

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1. Introduction

Aquatic humic substances (AHS) are polar, straw-colored, organic acids that are a principal component of aquatic organic matter (Thurman and Malcolm, 1981). They are chemically or biologically synthesized from biogenic substances or their degradation products (Aiken, 1985). AHS have a number of important biogeochemical functions: they control metal mobility and bioavailability in the aquatic environment (Bergamaschi et al., 2012) and regulate the attenuation of sunlight (Arts et al., 2000), thereby significantly

affecting primary production and the ensuing food web in the aquatic environment. The roles of AHS are undoubtedly dependent on their quality and quantity. A nonionic macroporous resin, Amberlite[®] XAD-8 (Rohm and Haas, Philadelphia, PA, USA), or its substitute, Supelite[™] DAX-8 (Supelco, Bellefonte, PA, USA), is used to isolate (e.g., Peuravuori et al., 2002; Thurman and Malcolm, 1981) or quantify (e.g., Leenheer, 1981; Tsuda et al., 2012; Van Zomeren and Comans, 2007) AHS in water, operationally defined as the hydrophobic fraction of dissolved organic matter that adsorbs onto the resins by lowering the pH to 2.

In general, AHS are operationally subdivided into two fractions: “dissolved” and “particulate” on the basis of the filter pore size (mostly 0.2–0.45 μm). In various aquatic ecosystems, the dominant pool of AHS in the water column occurs as a dissolved form. Because AHS have polyelectrolyte properties, both the fractions can

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transfer in either direction from one form to the other, depending on the water chemistry, such as pH and salinity. In most studies, the dissolved fraction has been selected as the subject of scientific interest after filtration of natural water. However, the effect of salinity on the adsorption behavior of these dissolved AHS onto the resin is yet to be confirmed. The theory of resin adsorption is that the hydrophobic part of the humic molecule sorbs or partitions into the resin matrix, an acrylic ester (Thurman, 1985). Although the non-conservative behavior of AHS as a function of salinity has been well established (e.g., Jones and Byran, 1998; Sholkovitz, 1976; Spencer et al., 2007), the remaining dissolved fraction of AHS that escaped aggregation, e.g., after mixing with sea water, has in general been overlooked. The size and conformation of AHS of the dissolved fraction can also be affected by the changes in salinity. Therefore, an increased salinity could modify the hydrophobic interaction between AHS and the nonionic resins, resulting in the possibility of salinity-induced changes in the values of quantified amounts or characteristics of AHS obtained from a salty system.

The aim of this study was to examine whether the quantified amounts of AHS using the nonionic resin would be affected by the changes in salinity or not. To achieve this goal, the reference fulvic acids (FA; the dominant components of AHS) samples from the International Humic Substances Society (IHSS) and Japanese Humic Substances Society (JHSS) with various chemical properties were dissolved in several concentrations of artificial sea water (ASW). A novel DAX-8 batch method (Tsuda et al., 2012) was used for the quantification of AHS in these solutions.

2. Materials and methods

2.1. Reference FA samples

In the present study, only FA were used because of the following two reasons: first, the majority of AHS in seawater, which were the subject of this study, occur as FA, approximately 90%, and 10% or less as humic acids (HA) (Malcolm, 1985; Thurman, 1985 and references therein); second, it is impossible to utilize HA to test the salinity effect using the DAX-8 adsorption method because all HA molecules inevitably precipitate in the acidic condition regardless of the solution salinity. For FA sample, Suwannee River FA (SRFA; Cat. No., 1S101F) and Nordic Lake FA (NLFA; Cat. No., 1R105F) were purchased from IHSS as the reference allochthonous, aromatic sample (aromaticity: SRFA, 0.33; NLFA, 0.46). As the reference autochthonous, aliphatic sample, Pony Lake FA (PLFA; Cat. No., 1R109F) and Lake Biwa FA (LBFA) were purchased from IHSS and JHSS, respectively (aromaticity: PLFA, 0.15; LBFA, 0.21). These four samples were isolated by the method described by Thurman and Malcolm (1981). Chemical properties of the IHSS reference FA and LBFA are presented online (<http://www.humicsubstances.org/index.html>) and by Fujitake et al. (2009), respectively.

2.2. Experimental procedure

An amount of 10 mg FA was put into a vial and 5 mL 0.1 M NaOH was added. After being completely dissolved, the solutions were stored in 1 L glass bottles to which 600 mL ultrapure water were added, generating $\sim 9 \text{ mgC L}^{-1}$ solutions. The sample pH was then adjusted to neutral (6.9–7.0) with dropwise addition of 0.1 M HCl. These procedures were conducted to ensure full expansion of FA molecules (Swift, 1989). Although NaCl was generated by neutralization, it was $<0.1 \times 10^{-2} \text{ M}$ and considered as trivial for this experiment. These solutions were then sterilely filtered through 0.2 μm membrane filter (JGWP, Millipore) on a clean bench to avoid biodegradation of the samples. Quintuplicate 110 mL aliquots of the filtrate of each sample solution were dispensed into 150 mL glass

bottles, to which an appropriate quantity of salts (NaCl, CaCl₂, and MgCl₂) was added in advance to obtain the solutions 0 (without salts), 1/4, 1/2, 3/4, and 1 times as high a concentration as that of ASW, respectively, which complied with Deslouis et al. (2006). The composition of ASW was as follows: NaCl: 0.5 M, CaCl₂: $1.05 \times 10^{-2} \text{ M}$, and MgCl₂: $5.5 \times 10^{-2} \text{ M}$. After the salts had completely dissolved, the solutions were kept for 48 h at 25 °C in the dark to be equilibrated and were filtered with a glass fiber filter (nominal pore size, 0.3 μm ; ADVANTEC GF-75, Toyo Roshi Kaisya, Ltd., Tokyo, Japan) to remove the precipitates. Thereafter, the filtrates were quantitatively analyzed for FA according to the method of Tsuda et al. (2012). Briefly, 0.4 mL of purified DAX-8 was put in a vial with a Teflon screw cap, and 20 mL of the water sample was added and acidified with 1 mL 1 M H₂SO₄ to adjust the pH to <2 . Note that the nonionic resin is able to adsorb AHS only in the acidic condition, which was the pH regulation for the AHS adsorption procedure in this study. After shaking for 24 h, the dissolved organic carbon (DOC) of the supernatant (non-AHS fraction) was analyzed by high-temperature combustion in a TOC-V_{CPH} analyzer (Shimadzu, Kyoto, Japan) through a 0.3- μm glass fiber filter. This was the fraction of AHS adsorption, performed in quintuplicate, in which non-AHS concentration was measured. Apart from that, the total DOM concentration of the sample without adding DAX-8 was measured. In short, AHS concentration was determined as the difference between the total DOM concentration ($\sim 9 \text{ mgC L}^{-1}$) and non-AHS concentration. All chemicals used were special grade; all glassware used was acid-washed and combusted at 450 °C for more than 3 h before use.

With respect to the FA concentrations, only one concentration was prepared for each sample because, although the conformation of FA in solution is governed by the sample concentration, pH, and ionic strength of the medium, the pH effect overwhelms the effect of the sample concentration when the pH of the medium is very low as in our study (<2) (Chen and Schnitzer, 1989). Hence, the concentration was determined in the range between at which the salinity effect can be noticeable and the method quantification limit of 36.9 mgC L^{-1} (Tsuda et al., 2012).

2.3. Statistical analysis

Differences in the quantified amounts (%) between the treatments were analyzed by one-way analysis of variance. Post hoc multiple comparisons of the treatment means were performed by Tukey's HSD, using the SPSS 17.0 statistical package for personal computers, and the level at which results were considered significant was $P < 0.05$ for all tests.

3. Results and discussion

The results of the quantification of the reference aliphatic samples (LBFA and PLFA) and reference aromatic samples (SRFA and NLFA) are shown in Table 1. There were not significant changes in DOC concentrations of LBFA and PLFA as a function of salinity, indicating that LBFA and PLFA did not aggregate by the addition of the salts. DOC concentrations of SRFA and NLFA decreased as salinity increased, which indicated that they aggregated along the salinity gradient and the aggregates were removed by subsequent filtration after equilibration. These differential responses to changes in salinity between aliphatic and aromatic FA were due to distinct chemical structural properties of them; however, this topic was not the subject of this study and not dealt with here to make the objective clear.

With respect to the adsorption experiment, LBFA and PLFA did not show significant salinity gradient changes in the rates of quantified amounts ($P < 0.05$). Conversely, the rates of the

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