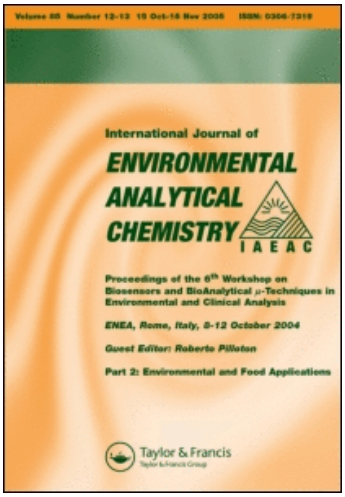

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PARTITIONING OF ANTIFOULING AGENTS, IRGAROL 1051 AND SEA NINE 211, TO HUMIC ORGANIC MATTER INVESTIGATED BY SOLID-PHASE MICROEXTRACTION

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The partitioning behavior of organic biocides onto humic organic matter (Fluka humic acids) was investigated. Solid-phase microextraction (SPME) was used in both direct and headspace approaches to measure the freely dissolved proportion of the target analytes rather than the proportion bound to the polymer. Data obtained with direct and headspace modes are very similar. Results indicated that Irgarol 1051 had the strongest adsorption characteristics and was found to bind more strongly to humic acids than Sea Nine 211. Obtained values are in good agreement with previously reported data, showing that these biocides are transported mainly in the dissolved phase of marine waters.

Keywords: Antifouling agents; SPME; Environmental analysis; Partitioning; Humic acids

INTRODUCTION

Following a ban on the use of tributyltin in antifouling products (IMO, 1998) on small boats a number of organic booster biocides have been utilized in antifouling paints as alternative treatments [1]. Among them, are Irgarol 1051 and Sea Nine 211, whose presence has recently been reported in the aquatic environment in several European areas at concentration levels ranging between 0.0025 and 3.3 μg/L for water samples [2–6] and between 1 and 1011 ng/g for sediment samples [2,7].

While large quantities of antifoulants enter the aquatic environment annually there is little information on their partitioning behavior in this environment. The environmental distribution and the fate of organic chemicals depend mainly on their sorption onto inorganic particulates such as clay minerals, oxyhydroxides and hydrous iron oxides and onto organic matter in sediments, soils and aquifers [8]. It is well established that dissolved and particulate organic matter changes the rate and transport of

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xenobiotics while the sorption process can change the bioavailability and toxicity [9]. Although partitioning of older biocides, such as organotin compounds, between particulate matter and water has been extensively investigated, as well as their sorption onto sediment or inorganic matrices [8,10–14], the sorption of the new "tin-free" biocides, such as Irgarol 1051 and Sea Nine 211 on dissolved organic matter has not been the subject of intense research.

Current methods used to determine available concentrations or study the binding of organic compounds to environmental matrices include fluorescence quenching [15], solubility enhancement [16], headspace equilibration [17], dialysis membranes [18] and Empore disks [19–21]. However, some of these methods are restricted to certain types of chemicals while others involve long equilibration/sampling time, and many of these techniques are laborious and involve multi-step manipulation. In addition, few of these methods are suitable to determine the free concentration in environmental samples, because they involve a significant depletion of the analyte (i.e., equilibria between the freely dissolved and the matrix-associated chemicals are disturbed).

Solid-phase microextraction (SPME) has become an alternative method for solvent-free extraction of analytes in recent years. Various methodological approaches such as direct [22,23], headspace [24] and derivatization [25,26] SPME, are appropriate for analyzing organic compounds covering a wide range of volatility and polarity. Although SPME has been predominantly utilized for analytical purposes, its application has been recently reported for investigating sorption phenomena [27–32]. The essential idea is based on the fact that only the free dissolved portion of the target analyte is taken up by the extraction fiber rather than the proportion that is bound onto the organic matter. Additionally to the ease of handling and the possibility of studying sorption on both particulate and dissolved humic organic matter (HOM) matrices, SPME has another advantage over traditional techniques: the sorption equilibrium is not significantly affected by the extraction because of the extremely small volume of the extracting phase (e.g., 0.025 μL for a fiber with 7 μm film thickness) [28].

Taking all this into account, the objective of the present work was to investigate the possibility of applying the SPME technique with both direct and headspace approaches for the determination of the partition coefficients between HOM (Fluka humic acids) and water for the antifouling agents Irgarol 1051 and Sea Nine 211.

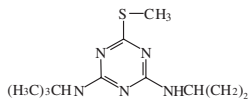
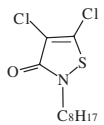
EXPERIMENTAL

Chemicals and Materials

Irgarol 1051 (2-methylthio-4-*tert*-butylamin-6-cyclopropylamin-*s*-triazine), was purchased from Ciba-Geigy (UK) and Sea Nine 211 (4,5-dichloro-2-*n*-octyl-4-isothiazolin-3-one) was a kind offer by Rohm-Haas (Philadelphia, PA, USA) (Table I). Analytical grade solvents were purchased from Pestiscan (Labscan Ltd, Dublin, Ireland) and humic acids were purchased from Fluka (Steinheim, Germany).

The SPME holder and PDMS (polydimethylsiloxane) fibers with a coating thickness of 7 μm were obtained from Supelco (Bellefonte, PA, USA). The fibers were conditioned at 270°C under helium overnight prior to use.

TABLE I Physicochemical properties of biocides

Biocide	*Chemical structure*	*Molecular weight* (amu)	*Water solubility* (mg/L)	*Henry*[a,b] *coefficient* (m^3 atm/mol) × 10^{-6}	$logK_{ow}$[b]
Irgarol 1051		253.36	7.0	0.42	3.95
Sea Nine 211		282.23	6.5	0.01	2.85

[a]Henry coefficients were estimated from the equation $K_H = P_i/S$, where S is the solubility in mg/L and P_i the vapor pressure; [b]K_{ow} is the octanol/water partition coefficients. Data from [33–35].

TABLE II Partition coefficients of biocides (literature and experimental data)

Biocide	*Log* K_{HA}		*Log* K_{oc}		
	Experimental[a]		*Normalized*		*Published*
	Direct	*Headspace*	*Direct*	*Headspace*	
Irgarol 1051	3.07 ± 0.19[b]	3.16 ± 0.09[b]	3.38	3.47	2.4–4.9[c]
Sea Nine 211	2.58 ± 0.26[b]	2.61 ± 0.11[b]	2.89	2.92	2.64[d]

[a]$C_{HA} = 100\,mg/L^{-1}$, $C_{biocide} = 20\,\mu g/L$, pH = 7.5; [b]Standard deviation from five replicates; [c]Log K_{oc} data from [33,37,38,42]; [d]Estimated from the equation $\log K_{oc} = \log K_{ow} - 0.21$ [36].

Sorption Experiments on Humic Acids (HA)

Partition coefficients between HA and water were determined for both analytes using a PDMS 7-μm fiber (Table II). A PDMS fiber was selected since it is generally considered to extract analytes via absorption due to its liquid phase. The 7-μm SPME fiber was used for the extraction of analytes because the extremely small volume of the extraction phase will avoid disturbing the sorption equilibrium [29].

HA stock solutions were prepared by dissolving humic acids in distilled water adjusted to pH 7.5. The target analytes were then spiked from a stock solution in methanol (100 mg/L) to obtain 20 μg/L per component in aqueous solutions.

The 40-mL amber vials were filled with 25 mL HA solution (100 mg/L) containing the target analytes, and sampling using the PDMS 7-μm fiber was conducted in the headspace after establishing the water/headspace equilibrium. Owing to the low Henry coefficients of the target analytes a long equilibrium time was observed (up to 36 h). Thus, a temperature of 30°C was chosen for the experiments in order to enhance the analyte evaporation rates and to achieve the equilibrium in a more reasonable time (24 h). Elevated temperatures (> 30°C) can shift sorption equilibration further away from typical environmental conditions [27] and were not studied in the present work.

For the direct SPME mode, 40-mL amber vials containing the analytes were completely filled in order to avoid headspace losses. During the extraction, the samples were continuously agitated with a magnetic stir bar at a constant rate of 960 rpm,

while the optimized conditions such as methanol content (0.1%) and desorption time (5 min) were as those described in previous work [39,40]. In order to investigate the influence of HOM on the extraction kinetics, spiked samples with analyte concentration of 20 μg/L were prepared with and without HOM and extracted for between 1 and 90 min. For the determination of K_{HA} values an SPME sampling time of 60 min was found to be sufficient to ensure sampling at equilibrium conditions (Figs. 1–4).

The freely dissolved portion was measured by SPME external calibration using distilled water with known concentrations of antifouling compounds (1–50 ppb) after 60 min extraction time (equilibrium time). The calibration was found to be linear in this range. Since the method assumes that the reduction in free concentration is only due to sorption to HA (quantitative recoveries from control samples after 24 h have shown that Irgarol 1051 and Sea nine 211 do not undergo dark reactions, such as hydrolysis and biodegradation), the total concentration of the samples was analyzed using liquid–liquid extraction [30]. The latter extraction was done by vigorously shaking 25 mL of the solution with 25 mL of *n*-hexane for 30 min in a 50-mL vial (no headspace

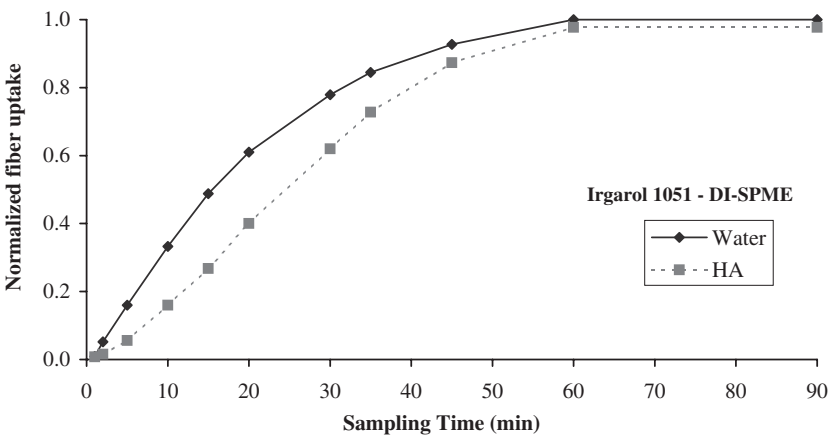


FIGURE 1 Direct SPME sampling of aqueous Irgarol 1051 solution (20 μg/L) from distilled water and water solution containing 100 mg/L HA.

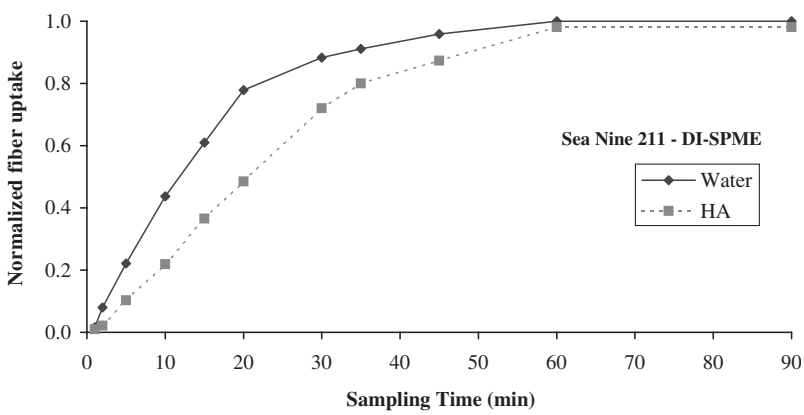


FIGURE 2 Direct SPME sampling of aqueous Sea Nine 211 solution (20 μg/L) from distilled water and water solution containing 100 mg/L HA.

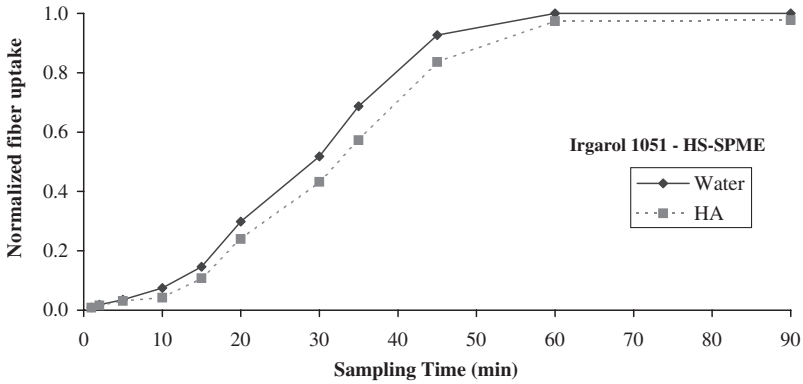


FIGURE 3 Headspace SPME sampling of aqueous Irgarol 1051 solution (20 μg/L) from distilled water and water solution containing 100 mg/L HA.

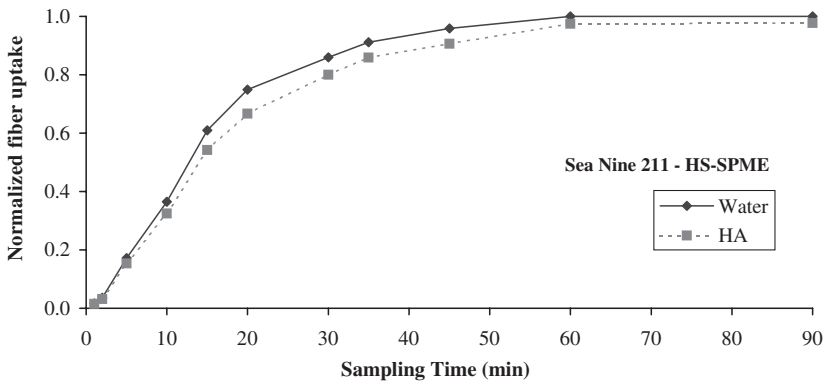


FIGURE 4 Headspace SPME sampling of aqueous Sea Nine 211 solution (20 μg/L) from distilled water and water solution containing 100 mg/L HA.

to avoid losses). The organic extracts were dried and concentrated by a gentle stream of nitrogen to a final volume of 0.5 mL. The stated K_{HA} values for each compound are averages of five replicates. GC-FTD and GC-ECD instruments were used for the analysis of Irgarol 1051 and Sea Nine 211 respectively.

Gas Chromatography

GC-FTD

Chromatographic analysis was performed using a Shimadzu 14A capillary gas chromatograph equipped with a flame thermionic detector (FTD) at 250°C. The DB-1 column, 30 m × 0.32 mm i.d., contained dimethylpolysiloxane (J & W Scientific, Folsom, CA). The temperature was programmed as follows: initial temperature was kept at 150°C for 2 min, which was increased to 200°C, at 5°C/min, held for 8 min, then raised to 210°C at 1°C/min and held for 2 min. The temperature was finally increased to 270°C at 20°C/min and held for 4 min. The injection temperature was 240°C. Helium was used as a carrier (1.5 mL/min) and the make-up gas (40 mL/min). The detector

gases were hydrogen and air, and their flow rates were regulated at 4 and 120 mL/min respectively. The SPME fiber was thermally desorbed for 2 min in the GC split/splitless injection port, held at 240°C. The injection port was in splitless mode.

GC-ECD

Chromatographic analysis was performed using a Shimadzu 14B capillary gas chromatograph equipped with a ^{63}Ni electron capture detector (ECD) at 300°C. Sea Nine 211 was separated using a DB-1 column, 30 m × 0.32 mm i.d., with a phase thickness of 0.25 μm. The temperature program used for the analysis was: from 80°C (2 min) to 290°C (10 min) at 21°C/min. The injection temperature was 240°C. Helium was used as the carrier at 1.5 mL/min and nitrogen was used as make-up gas at 30 mL/min.

RESULTS AND DISCUSSION

Extraction Kinetics

The influence of HA on the SPME fiber extraction kinetics was examined. Figures 1 and 2 illustrate the results of the measurements for the two biocides using the PDMS 7 μm fiber from distilled water and aqueous solutions containing 100 mg/L HA for direct extraction, and Figs. 3 and 4 the equivalent results for headspace extraction. In order to consider the different extraction kinetics due to the presence of HOM, the extracted amounts of antifouling compounds were normalized to the amount extracted when the extraction equilibrium was established. It is obvious that different extraction kinetics were observed for the PDMS 7 μm fiber with pure water and HA solution, for both biocides and for both direct and headspace SPME approaches. The HOM effects a retardation of the extraction probably due to an alteration of the stationary water layer around the hydrophobic fiber. These findings give strong evidence that SPME has to be applied under equilibrium conditions since other extraction times would lead to an underestimate of the sorption constants for the sorption of analytes to HOM [28].

Determination of K_{HA}

The determination of K_{HA} values were conducted both with the direct and the headspace SPME approach as described by Pöerschmann *et al.* [27–29]. Although both modes yielded almost identical results, from the methodological point of view the headspace approach might be more beneficial than conventional SPME in the present study, because possible fiber fouling by HOM adsorption can be excluded *a priori*.

The partition coefficients K_{HA} of biocides were calculated according to the following equation, as indicated by Poerschmann and co-workers [27]:

$$K_{HA} = \left(\frac{C_{total}}{C_{free}} - 1\right)\frac{1}{C_{HA}}, \quad (1)$$

where C_{free} and C_{total} are the concentrations of the analyte in the free dissolved state and in total, respectively, K_{HA} is the partition coefficient for the analyte between HA and water and C_{HA} is the concentration of HA in the sample (mg/L).

Table II gives $\log K_{HA}$ values for both biocides on humic acid calculated on the basis of Eq. (1). It is generally known that the sorption of hydrophobic compounds is strongly dependent on the content as well as the nature of the HA [41]. The determined partition coefficient to humic acids ($\log K_{HA}$) was directly correlated with the hydrophobicity of the compounds. Irgarol 1051, having the higher value of $\log K_{ow}$, was reasonably found to display a higher partition coefficient value ($\log K_{HA} = 3.07/3.16$ (Table II)). The normalized to organic content value ($\log K_{oc} = 3.48/3.56$ (Table II)) is in good agreement with the values published by Ciba ($\log K_{oc} > 3.56$) [42], Tolosa *et al.* ($\log K_{oc}$ 3.0) [37] and Bisseli *et al.* ($\log K_{oc} = 3.3 \pm 0.72$) [33] respectively, during the determination of water–sediment partition of the parent compound. On the other hand, higher variations between the calculated $\log K_{oc}$ values were found for Irgarol 1051 (2.41–4.89) in suspended solids (1–200 g/L) by Comber *et al.* [38]. It is worth noting that the K_{oc} value of Irgarol 1051 is higher than the K_{oc} value of other triazines such as atrazine and prometryne [43–44], possibly because of its higher hydrophobicity and lower solubility.

Sea Nine 211 reasonably displayed a lower $\log K_{HA}$ value than Irgarol 1051, indicating a lower sorption to HA which is in agreement with its low $\log K_{ow}$ value. Measured $\log K_{HA}$ values generated from this work show reasonable agreement with the theoretical values calculated in Table II. To our knowledge little literature data are available for the K_{oc} value of Sea Nine 211. Jacobson and Willingham (2000) have reported that this biocide has a high tendency to associate with sediment particles [35]; however, no values were provided in that study. In our work Sea Nine 211 showed a relative low tendency to partitioning to humic acids, which may be correlated with the characteristics of the humic materials.

The results presented above demonstrate that in the natural environment, where organic matter concentrations are likely to be lower that those investigated in the present study, the biocides will be predominately in the dissolved form. Thus they can be transported further in the water column making them more bioavailable.

CONCLUSIONS

The SPME method can be used to easily determine the partition coefficients of chemicals to environmental matrix components (e.g., HA, sediments), which are necessary to assess the environmental fate of pollutants. The partition coefficients of the biocides Irgarol 1051 and Sea Nine 211 to humic organic matter were estimated using a PDMS 7-μm fiber in both direct and headspace approaches, demonstrating similar results. We realize that Fluka humic acids are not comparable with natural humic acids, but this study focuses on the method itself and its applicability to environmental studies. The main advantages of the SPME technique over other techniques include its speed, that minimal manipulation of the sample is involved and that it is easily automated.

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