

instrumental conditions when the database was constructed. The results obtained from performance check standards (Naginata criteria sample mix 3: Hayashi Pure Chemical, Osaka, Japan) are evaluated against three criteria (Kadokami et al. 2004, 2005): spectrum validity, inertness of column and inlet liner, and stability of response. When the results for performance check standards satisfy the criteria, the difference between the predicted and actual retention times is less than 3 s, and chemical concentrations obtained (excluding some highly polar compounds which are difficult to measure by GC) are comparable to those obtained by conventional internal standard methods (Kadokami et al. 2005, 2009). After redissolving the sample in hexane (1 mL) and adding of internal standards (Naginata IS mix 3: Hayashi Pure Chemical, Osaka, Japan), the extract was analyzed by GC-MS (QP-2010Plus; Shimadzu, Kyoto, Japan). The GC-MS conditions are described elsewhere (Kadokami et al. 2004). Identification and quantification of the 940 or so semi-volatile compounds were finally performed by AIQS-DB. For full details of the extraction method and chemical determination, see Kadokami et al. (2005, 2009) and Jinya et al. (2013).

The instrument detection limit (IDL) for the chemicals in the database is typically ≤ 0.01 ng. Given a final determination adjusted by internal standard, analyte masses on disks correspond to residue concentrations reported as $\mu\text{g}/\text{disk}$.

3 Results and Discussion

The main objective of this pilot study was to explore the utility of the GC-MS-DB method in combination with passive sampling. In that context, the disk extracts were compatible with the GC-MS-database rapid screening technology, enabling 30 chemicals to be observed (Table 1), including pesticides, anti-oxidants, PAHs, solvents and plant steroids. For convenience, the 942 chemicals in the GC-MS multi-residue method are divided into groups based on their probable source. Grouping is, at times, somewhat arbitrary given that many of the wide range of chemicals covered in the GC-MS screen have multiple uses and therefore sources. For instance, octanol might be considered a solvent or a fragrance, and phenol either an industrial chemical or a disinfectant or a natural product. Some chemicals in the screen, such as the phthalates and petroleum hydrocarbons, are ubiquitous in the built

environment, including in laboratories, and their presence in reagent blank samples meant their presence on the CC disks could not reliably be assigned to real environmental contamination, and so such chemicals are not reported. Consequently, only a limited number of contaminants were reliably observed on the disks, perhaps reflecting the relatively uncontaminated waters into which most of the CCs were deployed. However, overall passive sampling using the CC system was eminently suited to providing field-concentrated samples for determination by the GC-MS-DB system.

There was little difference in the number of chemicals found in the disk extracts (SDB-XC, 18 chemicals; C18FF, 22 chemicals; Table 1) nor on the number of occasion residues were observed (SDB-XC, 41 detects; C18FF, 47 detects). For instance, there was little difference between the disks in the number of times one or zero chemicals were detected on the disks (SDB-XC, 67 % of analyses; C18FF, 62 % of analyses), and both disks were equally good for identification of (non)contaminated waters, with the data from both SDB-XC and C18FF disks highlighting the relative contamination of the city sites 16 and 17 compared to the rural sites (Table 2 and 3). Approximately half of all detected residues were observed on both disks, although the two disks did appear to have a tendency to sample chemicals with different polarity. For instance, the 22 chemicals sampled by the C18FF disk appeared more lipophilic than those sampled by the SDB-XC disk, although the variation in the data is such that there is no statistical difference between the two disks (C18FF average $\log K_{ow}$ of retained chemicals 4.0, range 1.4–9.7; SDB-XC average $\log K_{ow}$ 2.7, range -0.07 –6.1). The detection of a wide range of chemicals with radically different polarities using the two different receiving phases is consistent with Jinya et al (2013), who reported that the number and concentrations of chemicals observed after extraction of water samples using an Empore™ SDB-XD disk were almost identical to those obtained from the same samples using a cartridge-type SPE method and a liquid–liquid extraction method; in that case, the $\log K_{ow}$ values of the detected pollutants ranged from -0.07 (caffeine) to 14.6 (squalene).

Given the limited number of chemicals sampled by the CCs, it is natural to wonder whether this is due to an intrinsic property of the passive sampling system, or simply due to a lack of chemicals in the waters studied? Most of the waters studied are in peri-urban and rural

Table 1 Summary of the semi-volatile chemicals observed using the GC-MS-DB screening method (all sites; data pooled)

Chemical origin	Category	SDB-XC				C18FF			
		Detects ^a	<i>n</i> ^b	Mean	Range	Detects ^a	<i>n</i> ^b	Mean	Range
Agriculture		(μg/disk)				(μg/disk)			
	Insecticides	1/186	1	0.22	-	2/186	3	0.05	0.02–0.07
	Herbicides	2/120	6	0.16	0.04–0.37	2/120	4	0.15	0.09–0.21
	Fungicides	3/117	4	1.17	0.34–2.0	6/117	8	2.41	0.01–9.79
	Pesticide adjuvants	0/34	-	-	-	2/34	2	0.04	0.03–0.05
Business / household / traffic	Antioxidants	1/7	3	0.05	0.01–0.1	0/7	-	-	-
	Fire retardants	2/13	6	0.04	0.004–0.07	2/13	4	0.04	0.02–0.07
	Disinfectants (detergents) and phenols and metabolites	0/9	-	-	-	2/9	14	0.03	0.01–0.09
	Fatty acid methyl esters	0/36	-	-	-	1/36	4	0.04	0.04–0.05
	Fragrances and cosmetics	1/9	2	0.02	0.003–0.03	0/9	-	-	-
	Compounds from tyres	2/11	3	0.06	0.03–0.01	0/11	-	-	-
	Petroleum hydrocarbons	-/26 *				-/26 *			
	Plant or animal steroids	0/10	-	-	-	2/10	3	0.18	0.09–0.25
	Plasticizers	-/13 *				-/13 *			
	PPCPs	3/14	8	0.05	0.001–0.02	1/14	3	0.02	0.01–0.02
	Other	0/30	-	-	-	0/30	-	-	-
	Industry		(μg/disk)				(μg/disk)		
		Intermediates for dye manufacturing	0/26	-	-	-	0/26	-	-
	Intermediates for resins	0/11	-	-	-	0/11	-	-	-
	Intermediates for pesticides	0/6	-	-	-	0/6	-	-	-
	Intermediates in organic synthesis	0/59	-	-	-	0/59	-	-	-
	PAHs	2/47	6	0.01	0.002–0.02	0/47	-	-	-
	PCBs	0/62				0/62	-	-	-
	PCNs	0/28				0/28	-	-	-
	Solvents	1/17	2	0.01	0.005–0.02	1/17	1	0.02	-
	Explosives	0/6	-	-	-	0/6	-	-	-
	Others	0/39	-	-	-	1/39	-	-	-
	Total	18/942	41			22/942	47		

^aThe number of different chemicals in this class detected at least once

^bThe total number of detects of all chemicals in class; mean, average of detected concentrations

*n-alkanes from petroleum products and phthalate-base plasticizers were excluded because these compounds were detected in reagent blanks

areas, and there is little information on contamination by industrial and domestic organic chemicals in those waterways. In other words, in this case, we have no a priori information with which to judge the performance of the CC systems for more than half the chemicals in the GC-MS-AIQS-DB system. However, there is some information on pesticide contamination in the studied waterways. For instance, 98 pesticides were monitored at our study's sites in 2008–2009 using four gas

chromatography and two high-performance liquid chromatography-based analytical screens (Wightwick et al. 2012; Allinson et al. 2014; Schäfer et al. 2011). In that context, 32 pesticides were reported at one or more sites at low ng/L concentrations in September and October 2008, i.e. during the time our CCs were deployed. Eighty-seven percent of the pesticides in the six group-specific analytical screens used by Wightwick et al. (2012) and Allinson et al. (2014) are in the GC-

Table 2 Summary of site specific chemical residue determinations on SDB-XC disks (positive detects only; to two significant figures)

Class	Chemical	SDB-XC Site													
		1	3	4	6	11	13	16	17	18	19	20	23	24	
		(µg/disk)													
PAH	2,6-diisopropylnaphthalene	0.01				0.01			0.01						0.02
	naphthalene							0.00			0.00				
Fragrance	acetophenone		0.00					0.03							
Solent	isophorone							0.01	0.02						
Antioxidant	4-methyl-2,6-di-tert-butyl-phenol							0.10	0.02			0.01			
Tyre	2(3H)-benzothiazolone								0.10						
	benzothiazole							0.05	0.03						
Fire retardant	tributyl phosphate							0.05	0.03						0.00
	tris(2-chloroethyl) phosphate		0.04					0.07	0.03						
PPCP	caffeine							0.03	0.11						
	carbamazepine		0.20												
	diethyltoluamide		0.02		0.00			0.03	0.02		0.00				
Insecticide	pirimicarb										0.22				
Herbicide	prometryn												0.37		
	simazine			0.07	0.04		0.05	0.18	0.22						
Fungicide	iprodione										2.00				
	myclobutanil										0.34				
	pyrimethanil										0.01	0.02			

No detects at sites 2, 5, 9, 10, 14, 15, 21 or 22 using SDB-XC disk so these sites removed from Table; only detects are reported in this table

Table 3 Summary of site-specific chemical residue determinations (positive detects only; to two significant figures)

Class	Chemical	C18FF																
		Site # ^a																
		3	5	9	11	13	14	15	16	17	18	19	20	21	22	23	24	
		(μg/disk)																
Phenol	4-methyl-2,6-di-tert-butylphenol			0.01	0.01			0.01	0.09		0.03	0.03	0.04				0.07	
	nonylphenol		0.02						0.03	0.04		0.02	0.02				0.04	
FAME	methyldodecanoate						0.04						0.05	0.04			0.04	
B,H,T Other	3,5-di-tert-butyl-4-hydroxybenzaldehyde														0.02			
Plant steroid	β-sitosterol														0.25	0.21		
	cholesterol								0.09									
Solvent	octanol																0.02	
Fire retardant	tributyl phosphate								0.03	0.02								
	tris(2-chloroethyl) phosphate								0.07	0.05								
PPCP	diethyltoluamide	0.01							0.02	0.02								
Insecticide	fipronil										0.06							
	pirimicarb										0.07				0.02			
Herbicide	prometryn																0.15	
	simazine					0.09			0.12	0.21								
Fungicide	captan										0.09							
	iprodione										9.79	0.10			0.37			
	myclobutanil										1.01							
	procymidone										0.01							
	pyrimethanil										7.79							
	trifloxystrobin										0.14							
Pesticide adjuvent	fenpropathrin												0.03					
	oxabetrinil				0.05													

No detects at sites 2, 5, 9, 10, 14, 15, 21 or 22 using SDB-XC disk so these sites removed from Table; only detects are reported in this table

^aNo detects at sites 1, 2, 4, 6 or 10 using C18FF disk so these sites removed from table; only detects are reported in this table

MS-AIQS-DB screen used in this study. Almost all of the pesticides observed on the disks in this study were also observed in water samples by Wightwick et al. (2012) and/or Allinson et al. (2014). Moreover, all of the herbicides and fungicides (except procymidone) observed in this study were also observed in either SPMD solutions by Wightwick et al. (2012), or CC eluates by Allinson et al. (2014). The only pesticides observed on the SDB-XC disks used by Allinson et al. (2014), but not on the disks used in this study, were atrazine and hexazinone. Consequently, the CC system appears to have been sampling pesticides adequately, and the lack of industrial and domestic chemicals on the CC disks was most likely due to the relatively uncontaminated nature of most of the waters being surveyed.

Passive sampling has some advantages over grab water sampling in that the samplers need little attention apart from deployment and collection, and they also integrate and average exposures over time, thus enabling identification of events that may be missed by grab sampling (ITRC 2006; Gagnon et al. 2007). From a practical perspective, the in situ sampling and preconcentration obtained using passive sampling reduces the manual handling and breakage risks associated with transport of large numbers of large volume water samples in glass bottles from field to laboratory, and the number of laboratory operations required to obtain instrument-ready solutions for analysis. However, in natural waterways samplers may be subject to periodic high-energy flows, which can wash away the samplers, and be the subject of human inquisitiveness, which may see the samplers removed from the waterway; both these externalities can reduce the integrity of a sampling program, and both were experienced in this study. In addition, some chemicals may be missed, as they may not readily partition into the sampler, and once sampled, some chemicals may be desorbed into the water column. The major disadvantages, however, of passive sampling methods are that the data from the sampler may not be directly comparable to toxicity data based on water concentrations, and water concentrations may have to be extrapolated through the use of field or laboratory-derived sampling rates (R_s), few of which are available (Allinson et al. 2014). For instance, sampling rates are currently not available to derive time-weighted average water concentrations (TWAWCs) for most of the chemicals detected in the disk eluates. However, it was possible to estimate a field sampling rate for simazine (61 mL/day) using SDB-XC disk data for the sites

studied in Allinson et al. (2014). The TWAWC generated for simazine (0.07 $\mu\text{g/L}$) was approximately one fifth of the actual mean simazine concentration (0.37 $\mu\text{g/L}$) for the same sites reported by Allinson et al. (2014).

4 Conclusions

The main objective of this pilot study was to explore the utility of the GC-MS-DB method in combination with passive sampling. In that context, the disk extracts were eminently compatible with the GC-MS-database rapid screening technology, enabling 30 chemicals to be observed in the surface waters in and around Melbourne. From a practical perspective, the in situ sampling and pre-concentration reduces the manual handling risks associated with transport of large numbers of large volume water samples in glass bottles from field to laboratory, and the number of laboratory operations required to obtain instrument-ready solutions for analysis. The sources of the non-agricultural chemicals on the samplers is still unclear, but this study was conducted in a relatively dry season where total rainfall was approximately 40 % lower than the long-term mean in the catchment during the study period. Thus, the risks may be greater in wetter seasons, as greater quantities of chemicals are likely to reach waterways as the frequency, extent and intensity of surface run-off events increase. This study provides valuable information for policy and decision-makers, both in Australia and other regions of the world, in that passive sampling can be conveniently used prior to analysis by multi-residue techniques to produce data to assess the likely risks trace organic chemicals pose to aquatic ecosystems.

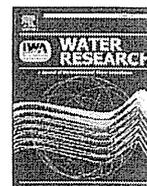
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Adsorption capacities of activated carbons for geosmin and 2-methylisoborneol vary with activated carbon particle size: Effects of adsorbent and adsorbate characteristics

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ABSTRACT

The adsorption capacities of nine activated carbons for geosmin and 2-methylisoborneol (MIB) were evaluated. For some carbons, adsorption capacity substantially increased when carbon particle diameter was decreased from a few tens of micrometers to a few micrometers, whereas for other carbons, the increase of adsorption capacity was small for MIB and moderate for geosmin. An increase of adsorption capacity was observed for other hydrophobic adsorbates besides geosmin and MIB, but not for hydrophilic adsorbates. The parameter values of a shell adsorption model describing the increase of adsorption capacity were negatively correlated with the oxygen content of the carbon among other characteristics. Low oxygen content indicated low hydrophilicity. The increase of adsorption capacity was related to the hydrophobic properties of both adsorbates and activated carbons. For adsorptive removal of hydrophobic micropollutants such as geosmin, it is therefore recommended that less-hydrophilic activated carbons, such as coconut-shell-based carbons, be microground to a particle diameter of a few micrometers to enhance their equilibrium adsorption capacity. In contrast, adsorption by hydrophilic carbons or adsorption of hydrophilic adsorbates occur in the inner pores, and therefore adsorption capacity is unchanged by particle size reduction.

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1. Introduction

Adsorption by activated carbon is the most widely used, simplest, and least expensive method for removing micropollutants, in particular hydrophobic compounds, in water treatment plants. The removal efficiency of micropollutants by activated carbon is related to the properties of the activated carbon: particle size, internal pore structure (pore size distribution), and pore surface chemistry (e.g., surface functional groups). The latter two characteristics have been intensively investigated with the goals of understanding adsorption phenomena and producing and selecting an appropriate activated carbon for a target micropollutant (Chesnut et al., 2007; Greenwald et al., 2015; Kilduff et al., 2002; Nowack et al., 2004; Rangel-Mendez and Cannon, 2005; Tennant and Mazyck, 2007; Watanabe et al., 2012). In contrast, the effects of

carbon particle size have not been fully investigated (Shi et al., 2014). Even though the pore surface chemistry of activated carbon is microscopically heterogeneous, activated carbon has generally been treated as a homogeneous adsorbent (Pami et al., 2008; Sontheimer et al., 1988; Weber et al., 1983); that is, its adsorption capacity was treated as being independent of the size of the carbon particles (Najm et al., 1990; Peel and Benedek, 1980; Randtke and Snoeyink, 1983). Therefore, particle size has been regarded as affecting adsorption kinetics and the time required for equilibration (Najm et al., 1991). However, the development of superfine powdered activated carbon (SPAC) generated by wet milling of commercially available powdered activated carbon (PAC) has revealed the importance of particle size with regard to adsorption capacity as well as kinetics (Cai et al., 2013; Delgado et al., 2012; Ellerie et al., 2013; Huang et al., 2009; Matsui et al., 2004; Wang et al., 2011). It has been reported that the adsorption capacity of activated carbon for macromolecules [for example, natural organic matter (NOM)] increases as the median particle diameter decreases

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from 10 μm (PAC) to 0.7 μm (SPAC), whereas the adsorption capacity for small molecules (for example, phenol) does not change with decreasing particle size (Ando et al., 2010). For 2-methylisoborneol (MIB) and geosmin, which are algal metabolites responsible for musty-earthly odor issues in public drinking-water supplies (Srinivasan and Sorial, 2011), adsorption capacity on coconut-shell-based carbons increases with decreasing carbon particle size, but it is independent of particle size for wood-based carbons (Matsui et al., 2009, 2012). However, the reason or mechanisms for why the adsorption of the small molecules MIB and geosmin depends on the particle size of carbon made from coconut shells are unknown. If carbons evidence such characteristics, grinding the carbon particles would greatly enhance the removal efficiency of MIB and geosmin in terms of adsorption capacity as well as kinetics. A study indicating that the magnitude of the dependence of the NOM adsorption capacity depends on the source of the raw material for the carbon (Ando et al., 2010) suggests that the size dependency of the MIB and geosmin adsorption capacity may be related to the properties of the carbon.

To explore the dependency of the adsorption capacity on particle size, we investigated the relationship between the properties of carbon and adsorbate molecules. Herein, we reveal the properties of carbon and adsorbates (including geosmin and MIB) related to the adsorption capacity dependency/independency on carbon particle size and discuss the nature of the mechanisms responsible for the particle size dependency/independency.

2. Materials and methods

2.1. Activated carbons

We investigated the dependency of the adsorption capacity on particle size for carbon samples obtained from various raw materials. Nine commercially available PACs derived from coconut shells, wood, and coal (Carbons A–I, Table 1) were slurried in ultrapure water (Milli-Q Advantage, Millipore Co.) and pulverized with a mortar and pestle or with wet bead mills (Metawater Co., Tokyo, Japan; Ashizawa Finetech Ltd., Chiba, Japan) to superfine particles (SPAC, diameter $<1.0 \mu\text{m}$) as well as to intermediate-size particles [Fig. S1 in the Supporting Information (SI)]. In this paper, we refer to these activated carbons as, for example, Carbon A (31.0) and Carbon A (0.50), where the numbers in parentheses indicate the median particle diameter in micrometers. The carbons were stored as slurries in ultrapure water at 4 $^{\circ}\text{C}$ and used after dilution and placement under a vacuum. The particle size distributions of the carbons were determined with a laser-light-scattering instrument (Microtrac MT3300EXII, Nikkiso Co., Tokyo, Japan) after the addition of a dispersant (Triton X-100, Kanto Chemical Co., Tokyo, Japan; final concentration, 0.08 vol %) and subsequent ultrasonic dispersion.

Carbon properties were characterized by (1) pore size distribution, (2) elemental composition, (3) content of acidic and basic functional groups (as measured by the Boehm technique) (Boehm, 1966), (4) pH of the point of zero charge (pH_{pzc}), and (5) pH at which the zeta potential was zero (the isoelectric point, IEP).

The BET (Brunauer–Emmett–Teller) surface areas and pore size distributions of the activated carbon particles were obtained by using the nitrogen gas adsorption–desorption method (Autosorb-iQ, Quantachrome Instruments, Kanagawa, Japan). The isotherm data for nitrogen gas desorption at 77.4 K were analyzed with the BET equation for BET surface areas; with the Barrett–Joyner–Halenda method for the mesopore region (pore diameter, 2–20 nm); and with the density functional theory method for the micropore region (pore diameter, 0.7–2 nm) (ASiQwin, ver.3.01, Quantachrome Instruments).

Elemental analysis was performed at the Hokkaido Research Organization, Industrial Research Institute, Japan. Carbon, nitrogen, and sulfur contents in $\sim 5\text{-mg}$ samples of activated carbon were determined with a CNOS Elemental Analyzer (Vario El III, DKSH Management Ltd., Tokyo, Japan). The oxygen content in $\sim 1\text{-mg}$ samples of activated carbon was determined with the same analyzer.

The amounts of acidic and basic functional groups on the internal surfaces of the carbons were determined by the Boehm technique (Biniak et al., 1997; Noh and Schwarz, 1990) as follows. An aliquot of 10 mL of 0.05 M NaOH or 0.05 M HCl solution was added to $\sim 0.2 \text{ g}$ of carbon, and the slurry was shaken, placed under vacuum for 1 h, and shaken again. After centrifugation of the slurry, the supernatant was filtered through a 0.2- μm membrane filter (DISMIC-25HP, Toyo Roshi Kaisha, Tokyo, Japan). Fifteen milliliters of HCl (0.05 M) or NaOH (0.05 M) solution was added to 5 mL of the filtrate, and the resulting solution was back-titrated with a solution of NaOH or HCl. For each carbon type, the measurements were conducted on the sample with the smallest particle size, for example, Carbon A (0.50). Measurements were not made on the other samples, because only limited amounts of the other samples were available.

We determined pH_{pzc} by the indirect titration method (Müller et al., 1985; Newcombe et al., 1993; Putra et al., 2009). The pH of a 0.01 M NaCl solution was adjusted to between 3 and 11 with 0.1 M HCl or 0.1 M NaOH, and the solution was allowed to stand for 48 h. An initial pH ($\text{pH}_{\text{initial}}$) was then measured, 0.15 g of carbon was added, and a final pH (pH_{final}) was measured after an additional 48 h. The pH_{pzc} value was determined as the pH at which the regression line for the experimental data ($\text{pH}_{\text{initial}}$ vs pH_{final}) crossed the line where $\text{pH}_{\text{initial}} = \text{pH}_{\text{final}}$.

IEPs were determined for carbon samples with median particle diameters of $<1.8 \mu\text{m}$, such as Carbon A (0.50). Large-particle samples, such as Carbon A (31.0), were unsuitable for zeta potential measurement because of their high settling velocity. Aliquots of

Table 1
Characteristics of activated carbons.

Designation	Median diameter (μm)		Raw material	Origin of as-received particles
	As-received particles	Ground particles		
Carbon A	31.0	2.56, 0.72, 0.50	Coconut shell	SP23, Pica
Carbon B	47.9	13.2, 1.93, 0.94, 0.57	Coconut shell	F-100D, Calgon Carbon Japan KK
Carbon C	10.6	0.49	Wood	SHW, Norit
Carbon D	15.4	1.55, 0.53	Wood	Taiko W, Futamura Chemical Co.
Carbon E	16.4	1.70, 0.83, 0.47	Wood	6WD, Calgon Carbon Japan KK
Carbon F	15.4	1.61, 0.55	Wood	Taiko W, Futamura Chemical Co.
Carbon G	25.2	3.10, 0.85, 0.52	Wood	MP23, Pica
Carbon H	18.9	4.93, 0.62	Wood	Taiko W, Futamura Chemical Co.
Carbon I	18.3	1.79, 0.95, 0.49	Coal	6D, Calgon Carbon Japan KK

Carbons D, F, and H had the same brand name but were assigned different designations because they were obtained from different lots in different years.

each carbon sample were added to solutions of various pH values at a final concentration of 20 mg/L. After each suspension was mixed for 8 h, it was injected into the cell of an electrophoretic light-scattering spectrophotometer (Zetasizer Nano ZS; 532-nm green laser, Malvern Instruments, Malvern, Worcestershire, UK); the zeta potential was measured at 25 °C three times, and an average reading was calculated.

2.2. Adsorbates and water samples

Stock solutions of MIB and geosmin were prepared by dissolving pure MIB or geosmin (Wako Pure Chemical Industries, Osaka, Japan) in ultrapure water and then filtering the resulting solution through a 0.2- μm pore size membrane filter. Organic-free water containing enough added inorganic ions to make the ionic composition equal to that of water from Lake Hakucho (Hokkaido, Japan) (Ando et al., 2010; Matsui et al., 2014) was spiked with the stock solutions to obtain an initial MIB or geosmin concentration of $\sim 1 \mu\text{g/L}$, because MIB and geosmin occur naturally at concentrations usually lower than $1 \mu\text{g/L}$. MIB and geosmin concentrations were analyzed with a purge-and-trap concentrator coupled to a gas chromatograph–mass spectrometer after geosmin- d_3 as an internal standard was added to the water sample (GCMS-QP2010 Plus; Shimadzu Corp., Kyoto, Japan; Aqua PT 5000 J, GL Sciences Inc., Tokyo, Japan). In addition to MIB and geosmin, we also tested seven other environmentally relevant compounds as supplementary adsorbates: dimethametryn, propyzamide, fenitrothion, acibenzolar-S-methyl, *m*-cresol (3-methylphenol), benzothiazole, and phenol. These compounds were selected to cover a variety of hydrophobicity based on their octanol–water partition coefficients (K_{ow}). Single-adsorbate solutions of these compounds were prepared by dissolving each pure chemical in organic-free water. The concentrations of these adsorbates were measured by spectrophotometry (dimethametryn: 223 nm, propyzamide: 207 nm, fenitrothion: 267 nm, acibenzolar-S-methyl: 253 nm, *m*-cresol: 269 nm, benzothiazole: 216 nm, and phenol: 269.5 nm).

2.3. Batch adsorption tests

In adsorption equilibrium tests, 150-mL aliquots of organic-free water spiked with an adsorbate were transferred to 160-mL vials. Activated carbons were immediately added to each vial, and the vials were manually shaken and then agitated on a mechanical shaker at a constant temperature of 20 °C for 1 week, which had previously been determined to be the time required to reach adsorption equilibrium (Matsui et al., 2012). We also conducted control tests by using multiple vials that did not contain carbon to confirm that adsorbate concentration changes during long-term mixing were negligible. After the water samples were filtered through 0.2- μm membrane filters, adsorbate concentrations in the aqueous phase were measured. Solid-phase adsorbate concentrations were calculated on the basis of mass balance.

3. Results and discussion

3.1. Dependence of adsorption capacity on carbon particle size

MIB and geosmin adsorption isotherms were obtained for nine activated carbons derived from various raw materials [Figs. S2 and S3 in the Supporting Information]. For MIB, the adsorption capacities of three of the activated carbons (coconut-based Carbon A and Carbon B and wood-based Carbon C) showed marked particle size dependence, whereas the adsorption capacities of the other carbons showed little or no particle size dependence. Typical isotherms for the size-dependent and size-independent cases are

shown in Fig. 1. The adsorption capacity of Carbon A increased when the particle diameter was decreased from 31.0 to 2.56 μm , but it did not change when the particle diameter was reduced further, to 0.72 or 0.50 μm . In contrast, the adsorption capacity of Carbon G was independent of particle size.

For the combination of geosmin and coconut-based Carbon A or Carbon B, SPAC showed markedly higher adsorption capacity than PAC; whereas for the other carbons, the adsorption capacities of SPAC were only moderately or slightly higher than those of PAC (Fig. S3 in the SI). Overall, the trend of the dependence of adsorption capacity on particle size, that is, a higher adsorption capacity on SPAC than on PAC, was clearer for geosmin than for MIB.

Ando et al. (2010) have reported that the adsorption capacity of carbon for macromolecules, specifically NOM with a molecular mass of $>3.1 \text{ kDa}$, depends on particle size. The results of this study confirmed that the change in carbon particle size did not result in any substantial change in internal pore size distribution, and therefore the dependency of the NOM adsorption capacity was not related to internal pore structure. We also confirmed that the adsorption capacity differences were not related to internal pore structure. Nitrogen adsorption–desorption analysis (Figs. S4 and S5 in the SI) did not show any marked difference in the pore size distribution between SPAC and PAC, even within the micropore region where MIB and geosmin molecules adsorb (Newcombe et al., 2002).

These investigators have also reported (1) that the adsorption capacity for a low-molecular-mass substance, phenol (98 Da), is independent of carbon particle size; (2) that the adsorption capacity for polyethylene glycols (saturated macromolecules) with a molecular mass of $\leq 3 \text{ kDa}$ is independent of particle size, whereas the adsorption capacity for polyethylene glycol with a molecular mass of 8 kDa depends slightly on particle size; (3) that the adsorption capacity for polystyrenesulfonates (unsaturated macromolecules), in particular high-molecular-mass polystyrenesulfonates, clearly depends on particle size; and (4) that among various types of NOMs, NOMs with a high specific ultraviolet absorbance show a stronger particle size dependence than NOMs with a low specific ultraviolet absorbance. On the basis of these results, we speculated that the dependence of adsorption capacity on carbon particle size might be a phenomenon associated with high-molecular-mass adsorbates with certain characteristics, such as adsorbates bearing unsaturated groups with chromophoric properties. However, geosmin and MIB are low-molecular-mass molecules (182 and 168 Da, respectively) without such properties. The results of the current study were therefore surprising. They suggested that the fact that a strong dependence of adsorption capacity on particle size was observed for some carbons but not for others was probably related not only to the properties of the adsorbate but also to the properties of the carbon.

3.2. Carbon property that determines the dependence of adsorption capacity on carbon particle size

The adsorption capacity dependence or independence on particle size can be quantified in terms of the penetration index, which is defined as the slope of a plot of the log of the median adsorbent diameter vs the log of the adsorption capacity (Matsui et al., 2011, 2012). However, this index was not applicable to MIB adsorption, because a particle size dependence of adsorption capacity was observed for Carbon A and B samples with particle diameters of $>3 \mu\text{m}$, but it was not observed for samples with particle diameters $<3 \mu\text{m}$ (Fig. 1 and Figs. S2 and S3 in the SI). This result implies that the adsorbate molecules do not completely penetrate the adsorbent particle, but instead they preferentially adsorb near the external surface of the particle. Direct visualizations of the

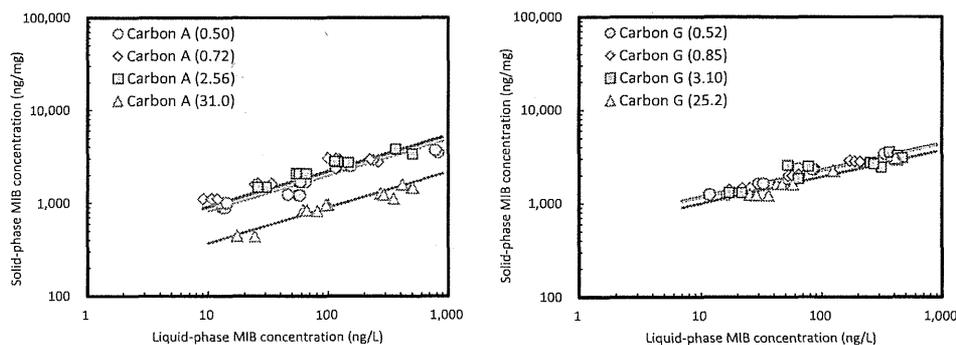


Fig. 1. Isotherms for adsorption of MIB on carbons A (left) and G (right). The lines represent fits to the shell adsorption model.

localization of micropollutant adsorbates in activated carbon particles actually provide evidence of the adsorption in the external region of carbon particles (Matsui et al., 2014; Obst et al., 2011). The shell adsorption model, Eqs. (1) and (2), is proposed to quantitatively describe the adsorbent particle size dependence of adsorption capacity: adsorption isotherms change with adsorbent particle size (Matsui et al., 2011):

$$q_E = K_{\text{overall}} C_E^{1/n} = C_E^{1/n} \int_0^R \int_0^R r^2 K_S(r, R) dr \left\{ \frac{3f_R(R)}{R^3} dR \right\} \quad (1)$$

$$K_S(r, R) = K_0 \times \{\max[1 - \alpha(R - r), 0] \times (1 - p) + p\} \quad (2)$$

where q_E is the equilibrium solid-phase concentration of the adsorbate (ng/mg); C_E is the equilibrium aqueous-phase concentration (ng/L); K_{overall} is the Freundlich adsorption capacity parameter [(ng/mg)/(ng/L)^{1/n}] for each carbon sample, e.g., Carbon A (0.50); n is the Freundlich exponent; r is the radial distance from the center of a carbon particle (μm); R is the carbon particle radius (μm); $K_S(r, R)$ is the radially changing Freundlich adsorption capacity parameter [(ng/mg)/(ng/L)^{1/n}] as a function of radial distance r from the center of a carbon particle (μm) and carbon particle radius R (μm); $f_R(R)$ is the normalized particle size (radius) distribution function of adsorbent (μm^{-1}); K_0 is the Freundlich parameter of adsorption at the external particle surface (i.e., the solid-phase concentration at $r = R$ at unity equilibrium concentration, [ng/mg]/[ng/L]^{1/n}); α is the reciprocal of the penetration depth (or the thickness of the penetration shell); and p is a dimensionless parameter that defines availability of internal porous structures for adsorption.

Eq. (2) says that local adsorption capacity in a carbon particle decreases linearly with distance from the external surface to a certain depth (penetration depth) and is a certain low value at depths exceeding the penetration depth. Therefore, when the carbon particle is small enough compared to the penetration depth, the entire interior region of the particle can be almost used for adsorption.

Eqs. (1) and (2) of the shell adsorption model were fitted to the experimental isotherm data. The fitting parameters were n , K_0 , and α (the p value was set at zero because of the model simplicity: actually this parameter was not needed for the MIB and geosmin isotherms to be modeled). These values were searched for each carbon, for example, Carbon A (the left panel of Fig. 1), by using a series of MIB adsorption isotherm data of various particle sizes. The fact that the model successfully described the dependence of adsorption capacity on carbon particle size shown in Fig. 1 and Figs. S2 and S3 in the SI supports the model, including the

assumption that the penetration depth ($1/\alpha$) is independent of activated carbon particle size.

The α values depended on the carbons, as shown in Table 2. We then searched for the carbon property that influenced the degree of penetration (adsorption capacity dependency) by plotting α against the various carbon properties listed in Table 2. For geosmin, α was most strongly correlated with the oxygen content of the carbon ($\rho = -0.94$ and $\rho^2 = 0.89$, Fig. 3), followed by sulfur and nitrogen contents and the numbers of basic functional groups (Fig. 2). For MIB, α was also most strongly correlated with the oxygen content of the carbon among others, but the ρ^2 value was not high ($\rho = -0.51$ and $\rho^2 = 0.26$, Figs. 2 and 4).

The oxygen content of the carbon has been shown to be positively correlated with the density of hydrophilic sites (de Ridder et al., 2013; Pendleton et al., 1997, 2002). For the geosmin adsorption, 89% of the total variation in the α value can be explained by oxygen content ($\rho^2 = 0.89$). The strong correlation between α and oxygen content therefore indicates that the hydrophilicity of activated carbon plays an important role in the dependence of the adsorption capacity on activated carbon particle size (Kim et al., 2005; Li et al., 2002). Moreover, the strong negative correlation ($\rho = -0.94$) indicates that α increases with decreasing carbon hydrophilicity; that is, the dependence of adsorption capacity on particle size becomes stronger with decreasing carbon hydrophilicity. For MIB, although a strong correlation to oxygen content was not observed, the correlation to oxygen content was the strongest among other carbon properties. According to the determination coefficient of 0.26, however, 26% of the total variation in the α values can be accounted for oxygen content. Therefore, the hydrophilicity of activated carbon may play a certain role for MIB in the dependence of the adsorption capacity on activated carbon particle size. The moderate negative correlation ($\rho = -0.51$) suggests that the dependence of adsorption capacity on particle size may become stronger with decreasing carbon hydrophilicity. The weaker correlation of MIB than of geosmin (Figs. 2–4) is possibly due to the difference in their hydrophobicity. The fact that MIB has slightly more polarity and a lower $\log K_{\text{OW}}$ (MIB: 3.31, geosmin: 3.57) may render it more amenable to adsorption inside the pores of less-hydrophilic carbons as described below (Cook et al., 2001).

3.3. Adsorption capacity dependence on carbon particle size for hydrophobic compounds

A dependence of adsorption capacity on particle size was also observed for other hydrophobic compounds, including dimethylmethyryl ($\log K_{\text{OW}} = 4.22$, molecular mass = 255 Da) and propylamide (3.57, 256 Da), as well as for geosmin (3.57, 182 Da) and MIB (3.31, 168 Da). However, a particle size dependence was not

Table 2
MIB and geosmin α values and carbon properties.

Carbon designation	Penetration distance of MIB (μm)	Penetration distance of geosmin (μm)	α of MIB (μm^{-1})	α of geosmin (μm^{-1})	BET surface area (cm^2/g)	Micro pore volume (mL/g)	Mesopore volume (mL/g)	Carbon content (wt %)	Nitrogen content (wt %)	Sulfur content (wt %)	Oxygen content (wt %)	Acidic functional groups (mequiv/L)	Basic functional groups (mequiv/L)	pH _{PZC}	IEP
Carbon A	4.2	3.1	0.24	0.32	1230 ± 60	0.44 ± 0.01	0.10 ± 0.02	85.2 ± 4.15	0.15 ± 0.03	0.08 ± 0.02	4.7 ± 0.84	582	448	8.11 ± 0.66	3.59 ± 0.25
Carbon B	6.1	3.0	0.16	0.33	1080 ± 60	0.39 ± 0.03	0.08 ± 0.02	89.16 ± 2.16	0.16 ± 0.03	0.09 ± 0.03	4.68 ± 0.85	329	208	6.87 ± 0.28	3.98 ± 0.12
Carbon C	4.0	6.6	0.25	0.15	790 ± 90	0.25 ± 0.03	0.26 ± 0.02	78.01 ± 2.01	0.24 ± 0.01	0.23 ± 0.03	6.88 ± 0.18	1140	214	8.56 ± 0.06	4.03
Carbon D	14.2	6.0	0.07	0.17	1110 ± 40	0.39 ± 0.01	0.11 ± 0.01	82.63 ± 0.69	0.19 ± 0.00	0.16 ± 0.01	7.34 ± 0.90	781	366	7.96 ± 0.56	2.82
Carbon E	22.7	8.7	0.04	0.11	1030 ± 100	0.36 ± 0.04	0.14 ± 0.02	85.85 ± 0.81	0.16 ± 0.01	0.12 ± 0.01	7.43 ± 0.99	711	440	8.61 ± 0.12	3.27 ± 0.27
Carbon F	>10000	9.6	0.00	0.10	1160 ± 30	0.39 ± 0.01	0.14 ± 0.01	85.39 ± 0.31	0.2 ± 0.02	0.21 ± 0.04	5.63 ± 2.00	ND	ND	7.83 ± 0.13	2.54 ± 0.21
Carbon G	31.4	5.0	0.03	0.20	1110 ± 60	0.38 ± 0.02	0.20 ± 0.02	87.64 ± 1.88	0.17 ± 0.02	0.12 ± 0.03	5.63 ± 2.00	790	365	9.2 ± 0.37	4.2 ± 0.03
Carbon H	11.4	7.4	0.09	0.13	1170 ± 80	0.40 ± 0.03	0.15 ± 0.01	82.57 ± 0.86	0.21 ± 0.01	0.13 ± 0.01	7.5 ± 0.93	696	568	7.81 ± 0.31	2.77 ± 0.09
Carbon I	13.5	10.1	0.07	0.10	910 ± 70	0.30 ± 0.03	0.12 ± 0.02	81.54 ± 1.72	0.4 ± 0.03	0.59 ± 0.06	8.69 ± 1.57	367	771	6.52 ± 0.12	4.29 ± 0.16
Regression analysis	—	—	Independent variables	Independent variables	Explanatory variables	Explanatory variables	Explanatory variables	Explanatory variables	Explanatory variables	Explanatory variables	Explanatory variables	Explanatory variables	Explanatory variables	Explanatory variables	Explanatory variables

The values of BET surface area, micropore volume, mesopore volume, carbon content, nitrogen content, oxygen content, acidic functional groups, basic functional groups, and pH_{PZC} are averages ± standard deviations obtained for particles of various sizes. Acidic and basic functional groups and some IEP values were measured only for the SPACs with the smallest particle sizes. Therefore, no standard deviations were calculated for these values.

observed for the hydrophilic compounds acibenzolar-S-methyl (1.90, 210 Da), benzothiazole (2.01, 135 Da), *m*-cresol (2.04, 108 Da), and phenol (1.46, 94 Da) (Fig. S6 in the SI). Fig. 5 shows the relationship between α and $\log K_{OW}$ (a hydrophobicity parameter) for these nine tested adsorbates. The strong positive correlation ($\rho = 0.88$ and $\rho^2 = 0.78$) clearly indicates that the adsorption capacity dependence observed for geosmin and MIB was due to their hydrophobicity. The dependence of adsorption capacity on carbon particle size was slightly larger for geosmin than for MIB (Figs. S2 and S3 in the SI). We infer that this difference reflects the fact that geosmin ($\log K_{OW} = 3.57$) is slightly more hydrophobic than MIB ($\log K_{OW} = 3.31$). Careful examination of Fig. 5 reveals that the α values of geosmin and MIB are higher than those of dimethametryn and propyzamide, even though the hydrophobicity (K_{OW} values) of dimethametryn and propyzamide are larger than those of geosmin and MIB. This result suggests that besides K_{OW} , other chemical properties such as molecular structure (Li et al., 2001) may also contribute to the high α values of geosmin and MIB.

Low-polarity compounds adsorb via physical mechanisms onto the inside of carbon pores, whereas polar compounds prefer to bond with active functional groups (Tennant and Mazyck, 2007). We infer that when low-polarity compounds ($\log K_{OW} > 3$) such as geosmin and MIB are transported from bulk water, they are tightly adsorbed in the pores near the outer surface of less-hydrophilic carbon particles and then may hardly penetrate inside the carbon particle. However, we have not reached clearer in-depth mechanism yet: further investigation is granted.

Because of the limited penetration distance of PAC particles, pores in the internal region of the particles are not available for adsorption of geosmin and MIB. Therefore, the lower hydrophilicity of PACs could be disadvantageous for high adsorption capacity. In contrast, it has previously been reported that the surface of less-hydrophilic carbons (carbons with lower oxygen contents) has a stronger affinity for MIB and thus adsorbs more MIB (Kim et al., 2005; Pendleton et al., 1997). For PACs, therefore, hydrophilicity (oxygen content) may not be a straightforward index of their adsorption capacities for geosmin and MIB. In fact, the oxygen content (hydrophilicity) of PACs was not correlated to either adsorption capacity or adsorption capacity normalized to internal pore surface (BET surface area), as shown in Fig. 6.

In contrast, because the radius of a SPAC particle is much smaller than the penetration distance ($1/\alpha$, Table 2), both the internal and the external regions of the SPAC particles can be utilized for adsorption. In that case, the chemistry of the pore surface should be the main determinant of adsorption capacity (Considine et al., 2001). In fact, the idea that a less-hydrophilic carbon (one with lower oxygen content) should adsorb more geosmin and MIB (Pendleton et al., 1997) was more true for SPAC than for PAC: the correlations between solid-phase adsorbate concentrations (adsorbate mass per unit BET surface) and oxygen contents were stronger for SPAC (Fig. 7) than for PAC (Fig. 6). This result indicates that the adsorption capacities of SPACs for geosmin and MIB are determined more largely by the hydrophilicity of the carbon, as indexed by oxygen content.

In the cases of activated carbons from some materials, the smallest particle size SPAC had a higher oxygen content than other SPACs and the PAC: among the other SPACs and the PAC, the oxygen contents were almost the same (Table S1 in the SI). These data for oxygen content suggest that the smallest particle size SPAC was more hydrophilic and would then have a lower MIB and geosmin adsorption capacity than the other SPACs and the PAC (Considine et al., 2001; Kim et al., 2005; Pendleton et al., 1997). However, such a trend was not apparent in the isotherm data (Figs. S2 and S3 in the SI): among the activated carbons of various sizes from the same material (e.g., Carbon A), a clear trend was not observed in the

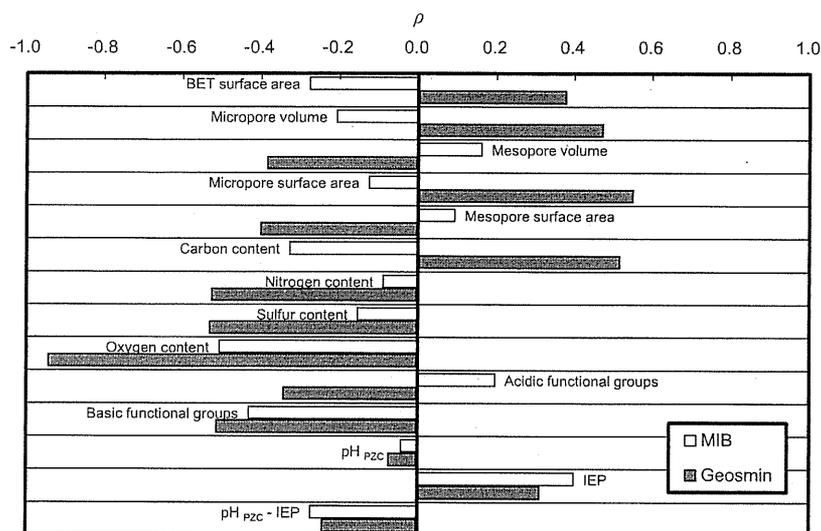


Fig. 2. Coefficients of correlation (ρ) between α and carbon properties.

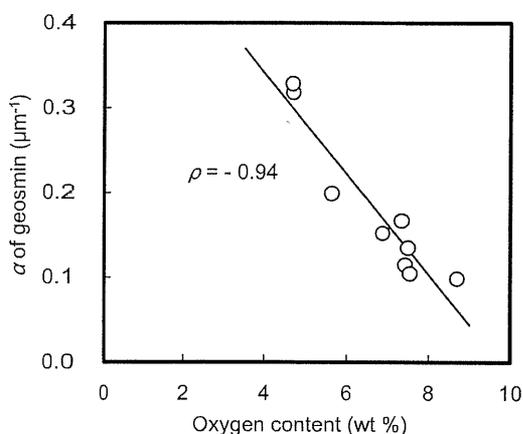


Fig. 3. Correlation between α of geosmin and oxygen content of carbon.

relationships between the quantity of MIB uptake (solid-phase MIB concentration) and the oxygen content of the activated carbon, although the oxygen content of each carbon was variable (Fig. S7 in

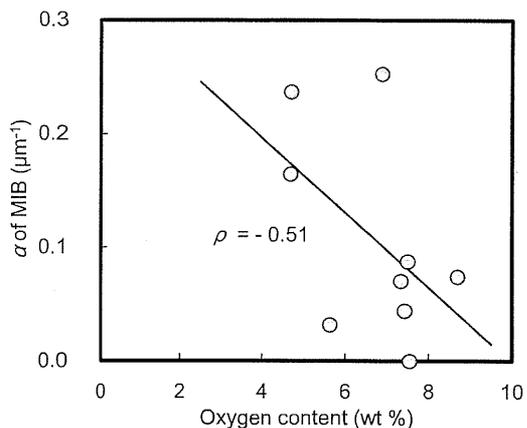


Fig. 4. Correlation between α of MIB and oxygen content of carbon.

the SI). One possible explanation for the variation of oxygen contents of each carbon might be an effect of particle size on combustion in the elemental analysis. Grinding carbon particles to a submicron diameter would expose the inside of the graphite core to the outer surface and might therefore render it more amenable to oxidation. Further study is needed of the change of elemental contents during grinding and its possible effect on geosmin and MIB adsorption.

4. Conclusion and implications

In the case of a hydrophobic adsorbate and a less-hydrophilic activated carbon (one with low oxygen content), the adsorbate molecule penetrates the carbon particles only to a certain distance. When the carbon particle radius is substantially larger than the penetration distance, the interior region of the carbon particle is not used, and equilibrium adsorption capacity increases with decreasing carbon particle size until the particle radius becomes much smaller than the penetration distance.

Therefore, for adsorptive removal of hydrophobic micropollutants such as geosmin, less-hydrophilic activated carbons, such as the coconut-shell-based carbons tested in this study (penetration distance, 3–6 μm), should be microground to a particle diameter of a few micrometers to enhance the equilibrium adsorption capacity for these hydrophobic micropollutants.

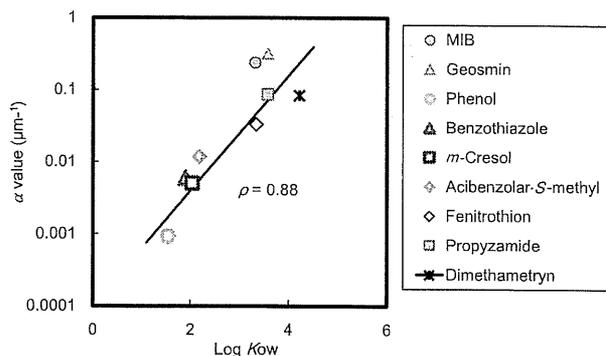


Fig. 5. Correlation between α and K_{ow} for various adsorbates on carbon A.

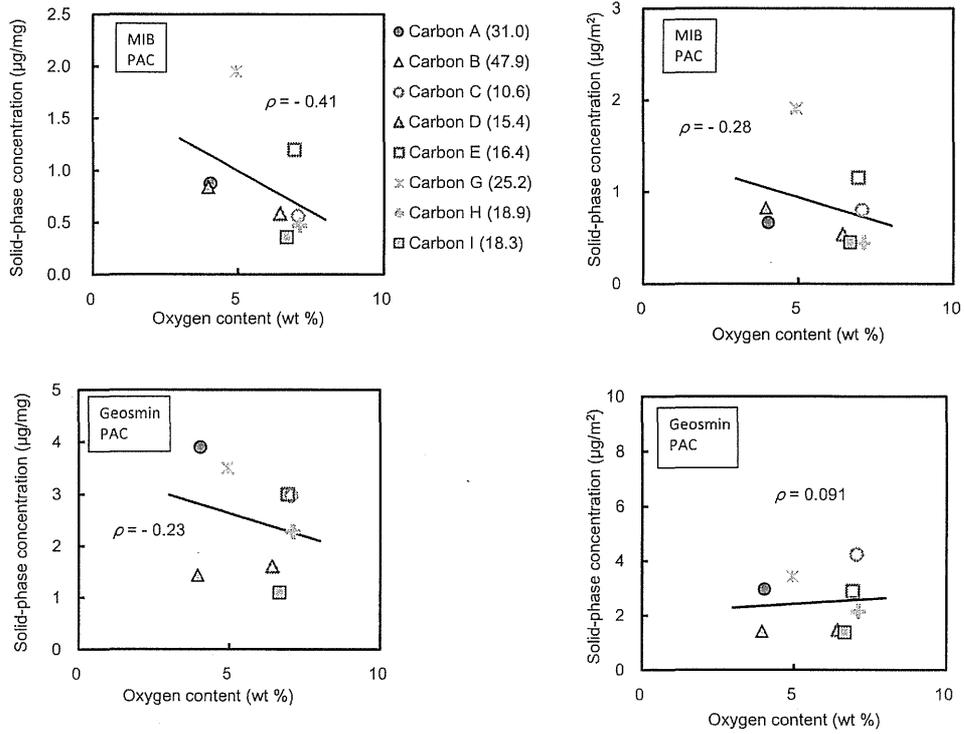


Fig. 6. Correlations between solid-phase adsorbate concentration for an equilibrium aqueous-phase concentration of 100 ng/L and PAC oxygen content for MIB (upper panels) and geosmin (lower panels). In the left panels, the values on the y-axis are adsorbate masses per unit mass of adsorbent, whereas in the right panels, the values are adsorbate masses per unit BET surface area of adsorbent.

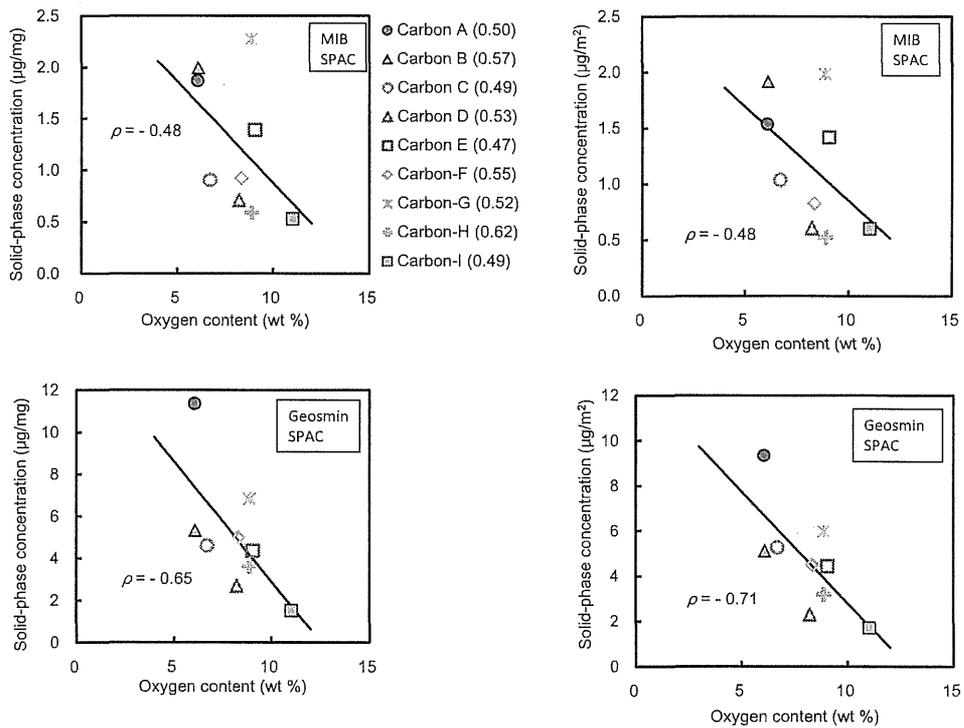


Fig. 7. Correlations between solid-phase adsorbate concentration for an equilibrium liquid-phase concentration of 100 ng/L and SPAC oxygen content for MIB (upper panels) and geosmin (lower panels). In the left panels, the values on the y-axis are adsorbate masses per unit mass of adsorbent, whereas in the right panels, the values are adsorbate masses per unit BET surface area of adsorbent.

When the particle radius is much smaller than the adsorbate penetration distance, as is the case for SPAC, the adsorption capacity is independent of particle size, and the chemistry of the pore surface is the main determinant of adsorption capacity. For SPAC adsorption of hydrophobic compounds such as geosmin, adsorption capacity per unit BET surface area is correlated with carbon hydrophilicity, as indexed by oxygen content. Selection of a less-hydrophilic carbon is therefore recommended for removal of hydrophobic compounds with a SPAC. In contrast, for a PAC, hydrophilicity may not be a straightforward index of adsorption capacity; the reason is that only part of the interior region of the carbon particle may be utilized because of the limited penetration of the adsorbate molecules, even though the pore surface has a strong affinity for the adsorbate.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.watres.2015.08.017>.

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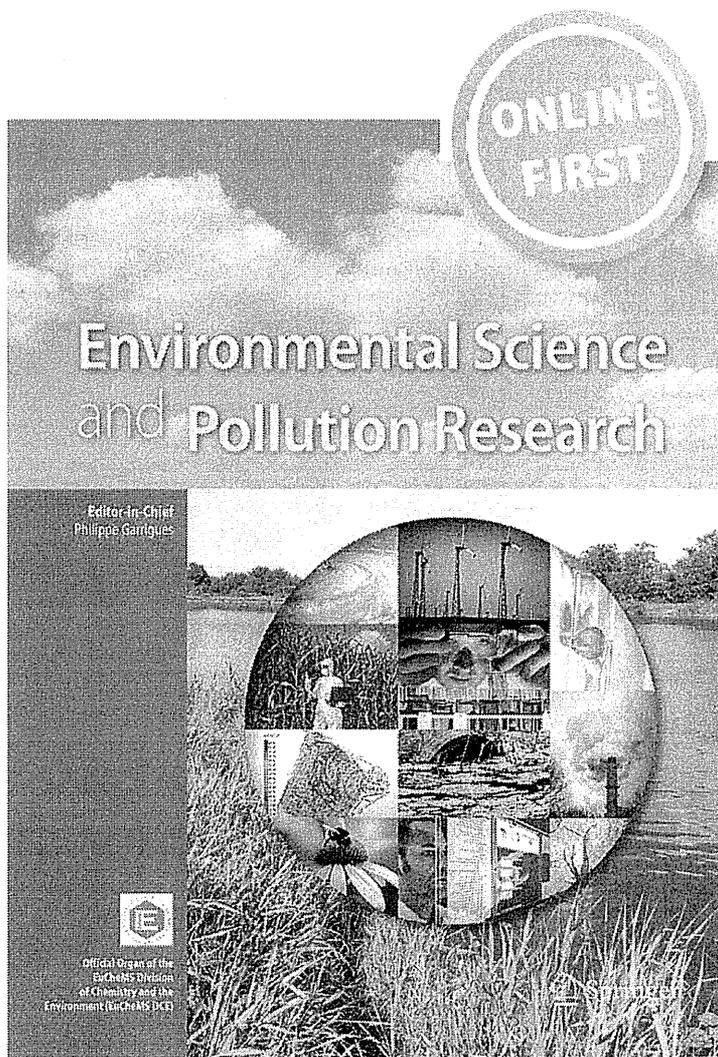
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RESEARCH ARTICLE

Groundwater screening for 940 organic micro-pollutants in Hanoi and Ho Chi Minh City, Vietnam

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Abstract Groundwater is the main source of drinking water for more than half of the residents of Hanoi (HN). It also provides about one third of the total water demand for residents of Ho Chi Minh City (HCM). However, due to rapid urbanization and frequent discharges of untreated urban wastewater to surface water, freshwater is widely contaminated by man-made chemicals, which may result in groundwater pollution. As part of an ongoing campaign to collect baseline information on the occurrence of organic micro-pollutants (OMPs) in the aquatic environment in Vietnam, 43 water samples were collected from 26 groundwater wells in HN (22) and

HCM (4) in September 2013 and August 2014. Samples were analyzed by gas chromatography-mass spectrometry (GC-MS) and the resulting chromatograms were screened for 940 OMPs by an automated identification and quantification system (AIQS) within a GC-MS database. A total of 74 compounds were detected, with between 4 and 43 (median 18) compounds found at each site. Overall, contamination levels were low, with over 89 % of the detected concentrations that were less than 0.5 µg L⁻¹. Results suggest that most of the sampled aquifers have been impacted by non-point source pollution. Most of the contaminants detected are either currently not regulated in drinking water or are present at low levels. A health risk assessment for detected contaminants implied that there were no risks to humans. Since this study was based on a limited number of samples, especially in HCM, further, more detailed studies on the occurrence of OMPs in groundwater in HCM and a full risk assessment of detected contaminants should be prioritized.

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Keywords GC-MS · Organic micro-pollutants · Comprehensive analysis · Groundwater · Occurrence

Introduction

Groundwater is an important source of water for industrial production and domestic use that has been a key driver for the geographical location and development of cities. Hanoi and Ho Chi Minh City, the two largest cities and most highly industrialized and urbanized areas in Vietnam, rely on groundwater to meet the high demand for freshwater. Huge amounts of groundwater are abstracted to meet the demands of residents, services, and industries. UNICEF (2001) reported that there were three types of groundwater exploitation in HN: (1) publicly exploited wells (large diameter) that are managed

by the Hanoi Clean Water Business Company and about eight major public exploitation wells that supply water to city treatment facilities, and which process 400 m³ of water per day; (2) private wells (500 medium diameter wells) that belong to businesses and factories and have a pumping rate of 120 m³ day⁻¹; and (3) 10,000 small diameter wells in four suburban districts sponsored by UNICEF that have a pumping rate of 30 m³ day⁻¹. The rural population of HN uses groundwater that is pumped from individual private (family based) tube wells as their source of drinking water. In HCM, high rates of industrialization and urbanization have resulted in a sharp increase in the demand for water. Out of the three sources of water (river water, groundwater, rainwater), groundwater use accounted for 34 % of the total water demand for HCM in 2005 (IGES 2007). Water is abstracted from over 150,000 wells or boreholes in HCM, demonstrating that groundwater makes an important contribution to the city's water supply (IGES 2007). In 2005, groundwater exploitation was estimated at about 611,000 m³ day⁻¹, of which 346,000 m³ day⁻¹ and 265,000 m³ day⁻¹ were used for domestic activities (residents, public works, and services) and industry, respectively (Nga 2006).

Just as vast quantities of freshwater are consumed, correspondingly large quantities of wastewater are produced that may, through various transport pathways, have an impact on the groundwater. Groundwater may suffer pollution from many sources. For example, groundwater in urban areas is likely to be impacted by pollutants from sewage, industrial activities, and diffuse leakages from reticulated sewerage and septic systems (Ellis 2006), while the main contributors to groundwater pollution in rural areas are probably fertilizers, agrochemicals, and veterinary medicines related to agriculture and animal waste (Boxall et al. 2004; Vázquez-Suñé et al. 2010). There have been many studies of heavy metals (especially dissolved iron(II), arsenic, and manganese), nitrogen compounds (nitrate and ammonium), and pathogens (coliforms) in groundwater of HN and HCM (Berg et al. 2001; Nga 2006; Buschmann et al. 2008; IGES 2007; Takizawa 2008). In these studies, the concentrations of some of the detected contaminants exceeded the Vietnamese Groundwater Standards and the World Health Organization (WHO) guidelines (IGES 2007; Buschmann et al. 2008).

Eighty thousand man-made chemicals are currently used in vast quantities in today's society (Schaidler et al. 2014) for a wide range of purposes including the production and preservation of food, industrial manufacturing processes, and for human and animal health care (Lapworth et al. 2012). In recent decades, there has been a growing interest in the occurrence, environmental fate, and potential toxicity of these so-called organic micro-pollutants in the terrestrial and aquatic environment (Kümmerer 2009; Carrara et al. 2008; Kishida et al. 2007; Swartz et al. 2006; Kolpin et al. 2002; Nhan et al. 2001; Daughton and Ternes 1999). These OMPs can make

their way into the aquatic environment by a variety of pathways such as direct discharges from wastewater treatment plants and landfills and application of human and animal waste to farmland (Barnes et al. 2008). However, while there is growing concern about groundwater contamination by OMPs, their fate and transport in groundwater remains relatively poorly understood compared with other types of freshwater pollution. Further, even with this concern, no comprehensive survey has been carried out in Vietnam to determine the extent of contamination by OMPs in groundwater.

In a previous study, we evaluated the occurrence of a range of OMPs (940) in surface waters and sediments in Vietnam (Duong et al. 2014a, b), including pharmaceuticals and personal care products (PPCPs); endocrine disrupting chemicals (EDCs); lifestyle compounds; sterols; persistent organic pollutants (POPs) such as organochlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs); pesticides; polycyclic aromatic hydrocarbons (PAHs); plasticizers; fire retardants; anti-oxidants; as well as numerous other compounds that originate from industrial and domestic sources. Two hundred and thirty-five and 185 analytes were detected in surface waters and sediments, respectively, indicating that the Vietnamese aquatic environment was contaminated by a wide range of OMPs. The findings suggested that the fate and transport of OMPs originating from households, such as sterols, EDCs, PPCPs, and pyrethroid insecticides in the environment, deserved greater attention from a research perspective. EDCs (such as bisphenol A (BPA), 4-tert-octylphenol (OP), and nonylphenol (NP)) have confirmed estrogenic potential even at low concentrations. In particular, elevated concentrations of OP in surface water may be hazardous as it can cause estrogenic effects in fish and other aquatic organisms. There is also concern about legacy POPs because of their persistence, accumulation in sediments, high bioaccumulation potential, and harmful biological effects. Some banned OCPs and PCBs remain at high concentrations in sediments. Concentrations of some plasticizers (such as phthalate compounds that are widely used in industrial production) and PAHs in sediments exceeded the standard values for protecting aquatic life, demonstrating that there may be toxicological stress on aquatic biota. In addition, Hoai et al. (2010) reported that 95 % of HN's wastewater effluents are discharged into its inner rivers without treatment. Hence, a large number of contaminants detected at elevated levels in Vietnamese surface waters and sediments may cause groundwater pollution. In spite of this, to date, there have been no comprehensive studies on the occurrence of OMPs in groundwater in Vietnam.

To address this knowledge gap, we undertook a comprehensive study of 940 OMPs, representing a wide variety of uses and origins, in groundwater from 26 wells in the two biggest cities in Vietnam, where previous research had demonstrated that surface water was heavily polluted by chemicals that originated from urban sewage discharges. The objectives

of this study were to (1) gain an overview of the occurrences and levels of OMPs in groundwater in Vietnam, (2) find potential sources of detected contaminants, and (3) to assess the potential risk of detected contaminants.

Materials and methods

Reagents and materials

All solvents used (acetone, dichloromethane, methanol, and n-hexane) were of pesticide residue quality and were purchased from the Kanto Chemical Co. (Tokyo, Japan). Reagents used for surrogate compounds and internal standards (IS) were purchased from the Kanto Chemical Co., Wako Pure Chemical Industries (Osaka, Japan), Wellington Laboratories (Ontario, Canada), and Sigma-Aldrich Japan K.K. (Tokyo, Japan) and were used in a $10 \mu\text{g mL}^{-1}$ acetone solution or in a $10 \mu\text{g mL}^{-1}$ hexane solution (IS). Sodium sulfate, disodium phosphate, and monosodium phosphate (99 % grade) were supplied by the Kanto Chemical Co. and were used to prepare a buffer solution of 1 mol L^{-1} $\text{NaH}_2\text{PO}_4\text{-Na}_2\text{HPO}_4$ (pH 7.0). Empore SDB-XD SPE disks (SDB polymer, 47 mm, XD) and Empore Activated Carbon SPE disks (47 mm, AC) were purchased from 3M Co. (St. Paul, MN, USA). Whatman GMF 150 glass fiber filters (47 mm) were purchased from GE Healthcare UK LTD. (Buckinghamshire, UK).

Water sampling

Samples were collected from groundwater wells in densely populated urban and suburban areas in HN and HCM. The wells were not necessarily used for drinking water but were thought to be contaminated from either unsewered household or industrial wastewaters, which suggested that the water may have been subject to organic pollution. Samples were collected twice in HN in the rainy seasons of 2013 and 2014 to examine if there was any variability in the occurrence and concentrations of the OMPs in the groundwater at different times of the year. A total of 22 samples were collected from 18 wells in HN and 4 wells in HCM in September 2013, while 21 samples were collected from 21 wells in HN (Fig. 1, Table S1) in August 2014. Overall, the samples were collected twice from 17 wells in HN. A bioassay test in September 2013 showed that samples from wells HN14 and HN3 had elevated concentrations and high toxicity values, so, in August 2014, samples were collected from four additional wells (HN3A, HN3B, HN14A, HN14B), located close to HN3 and HN14 (Fig. 1), and were investigated for OMPs as well as possible pollution sources. Samples were only collected once (September 2013) from one well in HN (HN3) and four wells in HCM (HCM1–4) because the wells were closed. Detailed

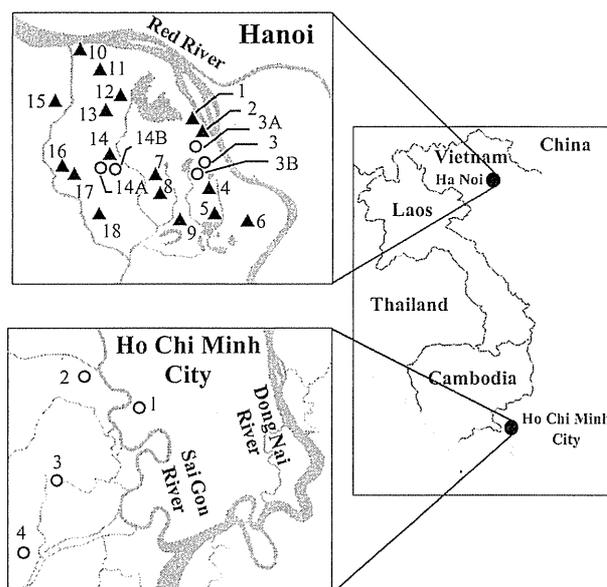


Fig. 1 Locations of the 26 wells sampled in Hanoi and Ho Chi Minh City. Two samples were collected (*triangle*) and only one sample was collected (*circle*). A detailed description of each well is provided in Table S1

information about the sampling locations is provided in Table S1 in the supplementary data.

Each well was pumped for 5 min before sampling to ensure that the water in the well was representative of the aquifer, and then, 1 L of a water sample was collected in a 1-L glass bottle, previously washed with acetone and purified water. Once collected, samples were labeled and stored in ice boxes and transported to a laboratory in the Institute of Environmental Technology (IET), Vietnam, where they were then refrigerated for 1–2 days until they were processed. Solid-phase extraction (SPE) of samples was carried out at the laboratory, and samples were kept in loaded SPE disks during transportation to Japan for further analysis.

Sample extraction and analysis

The groundwater samples were analyzed for 940 OMPs (Duong et al. 2014b) using the method of Jinya et al. (2013). Briefly, after addition of surrogates ($1 \mu\text{g}$) to 1 L of a water sample, the pH of the sample was adjusted to 7.0 with a phosphate buffer. The sample was loaded onto disks that had been previously pre-conditioned with dichloromethane, acetone, methanol (10 mL each), and water (20 mL) in the order: GMF 150, XD, and AC. After extraction, the disks were dried by applying a vacuum for 30 min. The disks were then eluted separately with 10 mL of acetone, 5 mL of dichloromethane (XD), and 10 mL of acetone (AC). The eluates were combined and finally concentrated to 1 mL under a gentle nitrogen stream and then was spiked with 100 μL of IS solution ($10 \mu\text{g mL}^{-1}$) prior to instrumental analysis (GC-MS selected ion monitoring (SIM)/total ion monitoring (Scan) (QP-2100