

Table 3 The MEC/PNEC ratios of detected compounds

Compound	MEC ($\mu\text{g/L}$)	PNEC ($\mu\text{g/L}$)	MEC/PNEC
Nonylphenol	26.9	0.21 ^a	128
Sulfamethoxazole	2.16	0.027 ^b	80
Ampicillin	0.64	0.075 ^c	8.6
Acetaminophen	5.64	1 ^b	5.6
Erythromycin	0.09	0.02 ^b	4.3
Clarithromycin	0.17	0.07 ^b	2.4
Sulfadiazine	0.11	0.135 ^b	0.8
Bisphenol A	7.82	11 ^a	0.7
Propranolol	0.13	0.244 ^b	0.5
Trimethoprim	0.18	2.6 ^b	0.1
Lincomycin	2.66	82 ^b	0.03
Roxithromycin	0.05	4 ^b	0.01
Atenolol	0.27	30 ^b	0.01
Cimetidine	0.19	35 ^b	0.01
Carbamazepin	0.03	13.8 ^b	0.002
Sulfapyridine	0.03	21.61 ^b	0.002

^a MOE 2001^b Verlicchi et al. 2012^c Kümmerer and Henninger 2003

(57 %), DBP (17 %), followed by caffeine and metformin (19 %).

Of the plasticizers, DEHP was detected at the highest concentrations ($>1 \mu\text{g/L}$ at each sampling location) of $19 \mu\text{g/L}$ (HCMC), $13.5 \mu\text{g/L}$ (Hanoi), and $13.0 \mu\text{g/L}$ (Red River), followed by bisphenol A (HCMC 7.82), DEP (HCMC 7.49, Hanoi 6.41), DBP (Danang 4.92, Red River 4.22, HCMC 3.24, Hanoi 1.45). Other studies have also suggested high detection frequencies ($>50 \%$) of these substances in surface waters but at higher concentrations. For example, Clara et al. (2010) reported DEHP with a detection frequency of 100 %, and maximum concentration of $34 \mu\text{g/L}$; DEP 100 %, $9.2 \mu\text{g/L}$; DBP 53 %, $8.7 \mu\text{g/L}$. Higher concentrations have also been reported in France, Germany, and Canada [DEHP: maximum $44 \mu\text{g/L}$, DEP $25 \mu\text{g/L}$ (Dagnat et al. 2009); DEHP $97.8 \mu\text{g/L}$, DBP $8.8 \mu\text{g/L}$ (Fromme et al. 2002); DEHP $70 \mu\text{g/L}$ (Barnabé et al. 2008), respectively].

In our study, we detected caffeine in surface waters at a maximum concentration of $13.0 \mu\text{g/L}$, much lower than the $91.6 \mu\text{g/L}$ reported by Duong et al. (2014) but higher than in other studies [$1.43 \mu\text{g/L}$ (Kong et al. 2014); $6.9 \mu\text{g/L}$ (Edwards et al. 2015)]. Another PPCP, metformin (an antidiabetic), was detected at the highest concentration compared with other PPCPs found in this survey (Hanoi $8.23 \mu\text{g/L}$ at maximum, HCMC $2.25 \mu\text{g/L}$), albeit these concentrations were more than two times lower than the maximum concentration found in a study in China ($20 \mu\text{g/L}$; Kong et al. 2014). Lower concentrations of metformin in surface waters have been observed in many developed countries, such as the

maximum 735 ng/L in France (Vulliet and Cren-Olivé 2011) and 1700 ng/L in Germany (Scheurer et al. 2009).

Environmental risk assessment of organic compounds

The ratios of the measured environmental concentration (MEC, maximum concentration in surface water) and the predicted no effect concentration (PNEC) were used to assess the environmental risk of detected compounds. The MEC/PNEC values were <1 indicating no toxic potential (Quinn et al. 2008). Of the 16 substances that were evaluated, six substances, nonylphenol (nonionic detergent metabolite), sulfamethoxazole, ampicillin, erythromycin, clarithromycin (antibiotic), and acetaminophen (analgesic), had MEC/PNEC >1 (Table 3). It indicates that these compounds are of concern and may warrant tier three toxicity assessment.

Conclusions

In the present study, 165 out of 1153 micropollutants examined were detected in surface waters, and of which more than 100 contaminants occurred at $\mu\text{g/L}$ level of concentrations in Hanoi and HCMC. Rivers in large cities were heavily polluted by a large number of organic microcontaminants, mainly from domestic sources such as PPCPs, plasticizers, and other household chemicals. Compared with large cities, Hue-Danang, the Red River, and Saigon-Dongnai River were less contaminated, and their pollutant sources were not just domestic but also agricultural and small-scale industries. The most frequently detected contaminants were plasticizers (DEHP, DEP, DBP, bisphenol A), dicyclohexylamine, and PPCPs (caffeine, metformin, cotinine). Their concentrations were high ($>1 \mu\text{g/L}$) higher than those found in international studies. One of the causes of serious pollution is that construction speed of sewage treatment plants does not catch up economic growth and urbanization. Therefore, accelerated construction of sewage treatment plants and enlightenment about chemicals are necessary to prevent expansion of pollution. Nonylphenol, sulfamethoxazole, ampicillin, acetaminophen, erythromycin, and clarithromycin had risk quotients (MEC/PNEC) >1 , suggesting these chemicals may be causing ecological harm, although further detailed field study is required to confirm this hypothesis.

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Combining Passive Sampling with a GC-MS-Database Screening Tool to Assess Trace Organic Contamination of Rivers: a Pilot Study in Melbourne, Australia

Graeme Allinson · Mayumi Allinson ·
Kiwao Kadokami

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Abstract This study assessed the suitability of passive sampler extracts for use with a GC-MS-database rapid screening technique for around 940 organic chemicals. Chemcatcher™ passive sampler systems containing either Empore™ SDB-XC or C18FF disks were deployed at 21 riverine sites in and near Melbourne, Victoria, Australia, for a period of 28 days during September–October 2008. Methanolic elution of the SDB-XC and C18FF disks produced an extract that, after evaporation and inversion into hexane, was compatible with the GC-MS-database method enabling over 30 chemicals to be observed. The sources of the non-agricultural chemicals are still unclear, but this study was conducted in a relatively dry season where total rainfall was approximately 40 % lower than the long-term mean for 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.

Keywords GC-MS AIQS-DB multi-residue method · SVOCs · Comprehensive analysis · Passive sampling · Yarra Valley · Victoria · Australia

G. Allinson · M. Allinson
Future Farming Systems Research Division, Department of
Environment and Primary Industries, DEPI Queenscliff
Centre, Queenscliff, Victoria 3225, Australia

G. Allinson (✉)
School of Applied Sciences, RMIT University, Melbourne,
Victoria 3001, Australia
e-mail: graeme.allinson@rmit.edu.au

M. Allinson
Centre for Aquatic Pollution Identification and Management
(CAPIM), School of Chemistry, The University of
Melbourne, Parkville, Victoria 3010, Australia

K. Kadokami
Faculty of Environmental Engineering, The University of
Kitakyushu, 1-1 Hibikino, Wakamatsu, Kitakyushu, Fukuoka
808-0135, Japan

1 Introduction

Managing the effects of trace organic chemical contaminants in waterways requires information, often far more than we (as scientists and/or managers) can afford to directly measure at all the places at all of the times, and for all the chemicals of interest. The measurement of nutrients and salts in surface and groundwater is now routine and offered cheaply by many commercial laboratories; however, this is not so for many other contaminants of concern, including many pesticides, pharmaceutical and personal care products (PPCPs) and industrial chemicals. Measurement of trace organic chemicals (TrOCs) in waters can be expensive in Australia, which inhibits monitoring by water authorities (as providers of water), catchment management authorities (as

custodians of the natural environment) and consumers (e.g. irrigators, industry and household and domestic water users), potentially resulting in increased risk to the natural environment. Strategies and/or tools are therefore required to focus monitoring and risk assessment programs in a cost-effective manner; the use of new sampling methods and preliminary screening of samples using rapid assessment tools are thus an increasingly attractive prospect for waterways managers.

When assessing organic substances, many analytical methods may have to be used to cover a large number of known compounds (Gómez et al. 2011), with concomitant financial implications associated with operating multiple, definitive chemical analytical screens using gas and/or liquid chromatography-based methods for volatile, semi-volatile non-polar and polar organic industrial, agricultural and domestic chemicals. In 2005, Kadokami et al. reported a new screening method that combined a mass-structure database with gas chromatography-mass spectrometry (GC-MS) to create a system that can screen samples for more than 940 semi-volatile compounds, including numerous halogenated and non-halogenated hydrocarbons, polynuclear aromatic hydrocarbons (PAHs), polychlorinated biphenyl compounds (PCBs), pharmaceutical and personal care products (PPCPs) and pesticides. The Kadokami et al. (2005) automated identification and quantification system with database (AIQS-DB) method was originally developed for screening unknown pollutants in environmental samples after incidents, e.g. fish kills, food contamination scares or the unknown number of harmful chemicals discharged into the environment after disasters such as large-scale fires and earthquakes, and has since successfully been applied to both water and sediment samples from rivers and estuaries in Japan (Kadokami et al. 2009; Pan et al. 2014), in Vietnam (Kadokami et al. 2012; Duong et al. 2014) and Victorian wastewater treatment plant effluents (Allinson et al. 2012). Consequently, when applied to river water, as in this study, this GC-MS-database (DB) method can give a good indication of the presence of some TrOCs that would not otherwise be identified if samples were to be subjected to only a very limited number of analytical screens for a limited number of target chemicals.

Collection of grab (or spot) samples is most commonly used to characterise TrOC residues in surface waters, although integrative sampling with passive samplers (or passive sampling) is becoming a more commonly used alternative. A 'passive sampler' can be

defined as a device that is able to acquire a sample from discrete location without the active media transport induced by pumping or purge techniques (ITRC 2006). Hence, most passive samplers consist of a receiving phase with high affinity for organic contaminants, separated from the aquatic environment by a diffusion limiting membrane. Some of the most commonly used devices that rely on diffusion and sorption to accumulate analytes in the sampler are semi-permeable membrane devices (SPMDs) and passive in situ samplers (such as the Chemcatcher™ system (CC)). Passive samplers had been little utilised on natural water samples in Australia at the inception of this study. In Victoria, one of the first detailed studies using passive samplers occurred between 2004 and 2006 when Rose and Kibria (2007) deployed SPMDs containing trimethyl pentane in irrigation canals in northern Victoria. The monitoring found three insecticides (endosulfan, chlorpyrifos and parathion methyl) in the passive sampler solvents. Elsewhere in Australia, a number of relatively recent studies have detected residues of atrazine, diuron, hexazinone and simazine in rivers and estuaries on the eastern seaboard of Australia using the CC passive sampling system (Escher et al. 2006; Muller et al. 2008; Shaw et al. 2009a, b, 2010; Stephens et al. 2009; O'Brien et al. 2011), and Mueller et al. (2011) tracked POPs in the Brisbane River, but prior to this study, there had been no significant studies investigating TrOCs in surface waters in Victoria using the CC system.

The sampling rates of chemicals into passive samplers are dependent on a range of factors, both intrinsic to the passive samplers themselves and extrinsic factors (Leonard et al. 2002). Extrinsic environmental factors that may affect uptake include flow rate, water temperature and changes in the sorptive properties of the water (due to dissolved organic matter and suspended particulates; Leonard et al. 2002). Intrinsic factors that may affect uptake include the polarity of the contaminant (as measured by its octanol-water partition coefficient, K_{ow}), the diffusivity of the molecules that have to pass through the aqueous boundary layer, sampler design, exposure time and concentrations of chemicals in the surrounding water. Perhaps of most importance is the type of receiving phase used in the passive sampler relative to target analytes, and whether the receiving phases are used with rate limiting membranes or without them ('naked'). The purpose of rate limiting membranes is literally that suggested by their name—to reduce the rate at which chemicals are adsorbed by the receiving

phase. For instance, the sampling rates (Rs) reported by Shaw et al. (2009a, b) when using naked sulphonated polystyrene divinylbenzene-reverse phase sulphonated disks (Empore™ SDB-RPS disks; Rs: atrazine 0.44 L/day; simazine 0.36 L/day) were about three times higher than when the same experiment was conducted with SDB-RPS disks and a polyether sulphone (PES) membrane (Rs: atrazine and simazine, 0.140 L/day). By reducing the sampling rates, the length of time before all available sites in the receiving phase are saturated is increased. This in turn allows for lengthier exposure periods in the field. In that context, SDB-RPS disks were used naked for 10 days for monitoring a polar herbicide (amitrole) in New South Wales by Sánchez-Bayo et al. (2013), whereas Allinson et al. (2014) were able to use Empore™ SDB-XC disks covered by a PES membrane for 28 days to target similarly polar herbicides in Victorian surface waters. At the inception of this study, receiving phases appeared to be being chosen by expert opinion based on their use to extract target analytes from water samples in the laboratory, although since that time, there has been some systematic study comparing the performance of different receiving phases in the field (e.g. SDB-RPS, SDB-XC and C-18 disks for the monitoring of nonylphenoethoxylates and nonylphenol in aquatic ecosystems; Ahkola et al. 2014).

In recognition of the potential risks that TrOCs pose to aquatic ecosystems, and the lack of information on the levels of such chemicals in Victorian freshwaters, this study was initiated to compare the utility of two different, but common receiving phases for the CC passive sampler system under field conditions in conjunction with a ‘single-shot’ multi-residue testing method. To that end, CCs were deployed at 21 sites in urban, peri-urban and rural waterways in and around Melbourne in September–October 2008 and retrieved samples prepared for measurement of approximately 940 semi-volatile organic chemicals by GC-MS-DB.

2 Materials and Methods

2.1 Study Sites

Twenty-one sites were monitored in and around Melbourne for this study (Fig. 1), which was conducted independent of, but in conjunction with a larger, complementary multi-disciplinary study of waterways in and around Melbourne. In that context, this manuscript

is a companion piece to the papers by Wightwick et al. (2012, 2013) and Allinson et al. (2014) who reported the levels of fungicides, metals and herbicides, respectively, in the surface waters and sediments in riverine ecosystems in the Middle and Upper Yarra catchment area, some of which were used for this study. The sites were selected for a variety of reasons: either because they were already part of Melbourne Water’s Yarra River water quality monitoring program (e.g. site 23), were in a section of very high regional importance (as defined by PPWRRHS 2007; e.g. site 18), were downstream of a tributary with of very high regional importance (e.g. site 1), downstream of a tributary with known industrial pollution or waste water treatment plant (WWTP) impacts (e.g. site 3, 16, 17) or being sampled as part of other concurrent Melbourne Water funded research (e.g. sites 22, 23 and 24 used by Schäfer et al. 2011).

Most of the study sites (75 %) were within the Yarra River catchment, with two study sites on the Mornington Peninsula and two sites in an agricultural location in the Barwon River catchment (sites 22, 23 and 21, 24, respectively). The Yarra River watershed is approximately 4000 km² and home to approximately 2 million people in the city of Melbourne (the capital and most populous city in the state of Victoria). The city is located at the northern-most point of a large natural bay (Port Phillip Bay), with the city centre itself positioned on the estuary of the Yarra River (Fig. 1). The metropolitan area extends along the eastern and western shorelines of Port Phillip Bay and more than 25 km inland. The Yarra River flows 240 km from its headwaters to the sea in Port Phillip Bay, and, in general, water quality is good in the upper catchment, but deteriorates downstream because of diffuse pollution from changed land use, particularly from agriculture and urban development (PPWRRHS 2007). Specifically, the upper sections of the Yarra River and its main tributaries (above site 1; Fig. 1) flow through forested, mountainous areas that have been reserved for water supply purposes for more than 100 years. Most of the land in the upper-middle section (above site 1) has been cleared for agriculture, although there is significant peri-urban development. The land downstream of site 1 is primarily urban and industrial. The lowest 10-km section of the Yarra River is estuarine. In the urbanised area of the Yarra River catchment, stormwater has a major impact on the river’s water quality. Several small (10,000–50,000 population equivalents) wastewater treatment plants (WWTPs) discharge treated effluent into the Yarra River (either

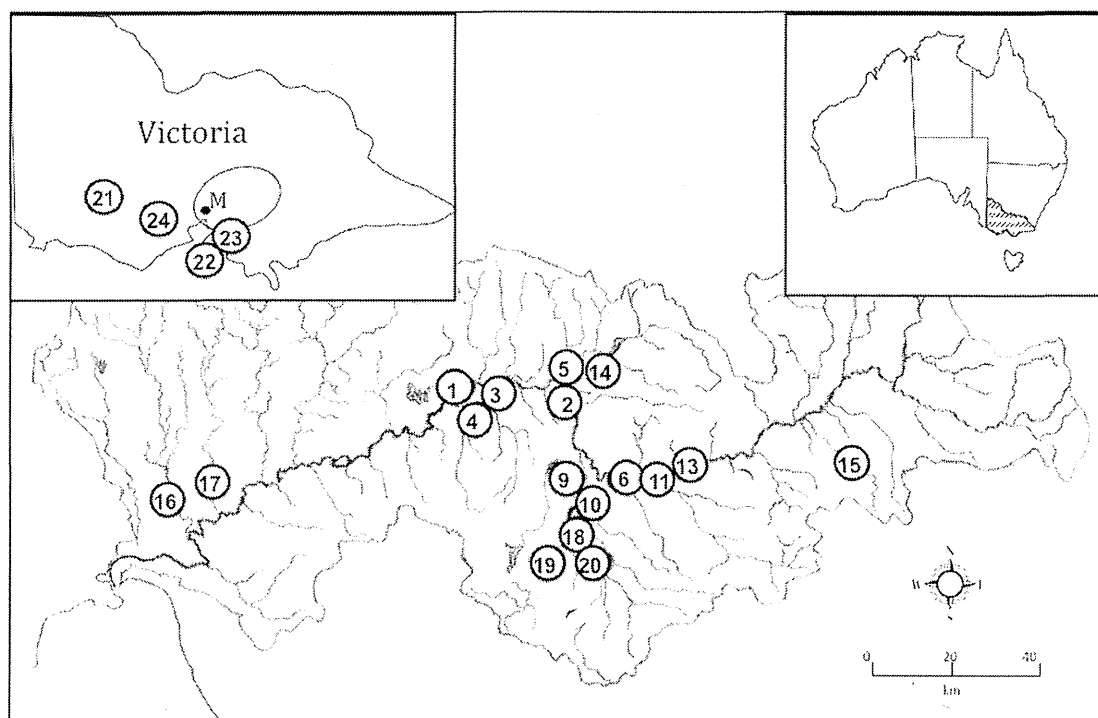


Fig. 1 Approximate location of sampling sites in and around the city of Melbourne (M) in the Yarra River catchment (oval outline), Barwon River catchment (sites 21 and 24) and on the Mornington Peninsula (sites 22 and 23), in Victoria, Australia

directly or via a tributary), although most of Melbourne's domestic and industrial sewage is transferred to two large WWTPs in the south and west of the city and after treatment discharged to the ocean.

2.2 Passive Sampling

A single type of passive sampler was used in this study, namely the Chemcatcher™ passive sampler system (CC). The CC system consists of machined polytetrafluoroethylene (PTFE) body that protects the chromatographic receiving phase (see Kingston et al. 2000). In this study, the CC system was fitted with either an Empore™ SDB-XC disk or an Empore™ C18FF disk (47 mm; 3 M, MN, USA) as the receiving phase and a polyethersulfone (PES) membrane (Sterlitech Corp, WA, USA) as the diffusion-limiting membrane. The SDB-XC and C18 disks were conditioned by soaking them in methanol (1 h) after which they were rinsed with deionised water on a disk extraction manifold; the PES membranes were conditioned in 50:50 methanol/water for 1 h then deionised water for 1 h. Samplers containing the two types of receiving phases were deployed in October 2008 for time-integrated monitoring to allow first a qualitative assessment (i.e.

presence/absence) and then, where possible, a semi-quantitative assessment (i.e. based on estimated time-weighted average water concentrations) of semi-volatile chemicals in the catchment. For full details of CC preparation and field deployment, readers are directed to the Supplementary Information in Allinson et al. (2014).

Passive samplers were disassembled at DEPI Queenscliff Centre, and the receiving disk and PES membrane dried at 35 °C on a hotplate for approximately 1.5 h. Each disk was wrapped separately in aluminium foil, labelled, placed inside another labelled plastic bag and stored at 4 °C until analyte elution. One disk from each of the site replicates was haphazardly chosen and was eluted with methanol (5 mL) into a glass tube and the resulting solution evaporated to dryness with N₂. The samples were reconstituted in hexane (1 mL), and in this dissolved form, the sample was transported to the University of Kitakyushu for multi-residue screening.

The AIQS-DB method identifies and quantifies chemical substances by using a combination of retention times, mass spectra and internal standard calibration curves registered in the database. In order to obtain accurate results, a GC-MS has to be adjusted to designated conditions that are almost the same as the

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						
	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 (TAWACs) 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 TAWAC 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.

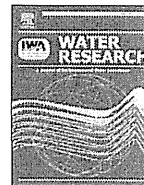
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Adsorption capacities of activated carbons for geosmin and 2-methylisoborneol vary with activated carbon particle size: Effects of adsorbent and adsorbate characteristics

Yoshihiko Matsui^{a, *}, Soichi Nakao^b, Asuka Sakamoto^b, Takuma Taniguchi^b, Long Pan^b, Taku Matsushita^a, Nobutaka Shirasaki^a

^a Faculty of Engineering, Hokkaido University, N13W8, Sapporo 060-8628, Japan

^b Graduate School of Engineering, Hokkaido University, N13W8, Sapporo 060-8628, Japan

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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 Mazzyk, 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 (Patni et al., 2008; Southeimer 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

* Corresponding author.

E-mail address: matsui@eng.hokudai.ac.jp (Y. Matsui).

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 μm) 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 ~5-mg samples of activated carbon were determined with a CNOS Elemental Analyzer (Vario El III, DKSH Management Ltd., Tokyo, Japan). The oxygen content in ~1-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 (Bimak 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 ~0.2 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 μm , 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	GWD, 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 ~ 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 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 ≤ 3 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 μm , but it was not observed for samples with particle diameters <3 μm (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

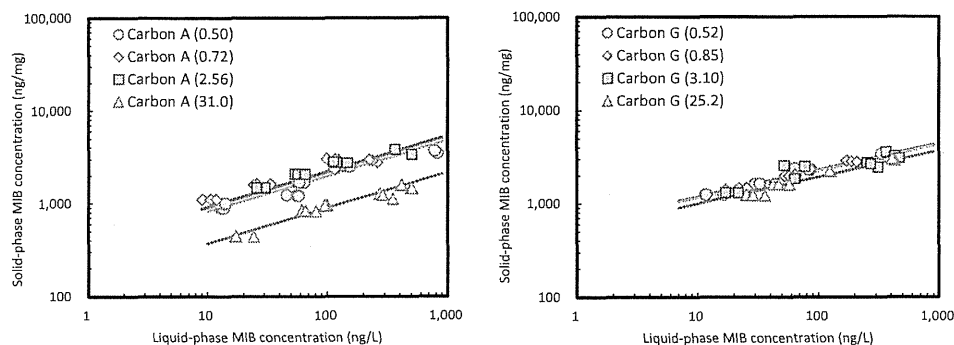


Fig. 1. Isotherms for adsorption of MIB on carbons A (left) and G (right). The lines represent fits to the shell adsorption model.

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):

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

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

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 dimethylametryn ($\log K_{\text{OW}} = 4.22$, molecular mass = 255 Da) and propylzamide (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)	Micropore 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	7.54 ± 0.53	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 propylamide, even though the hydrophobicity (K_{OW} values) of dimethametryn and propylamide 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., 2002) 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

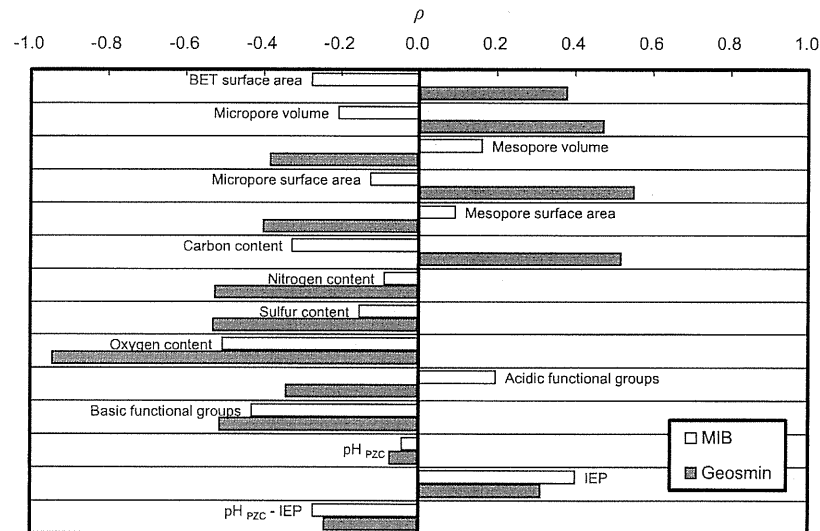


Fig. 2. Coefficients of correlation (ρ) between α and carbon properties.

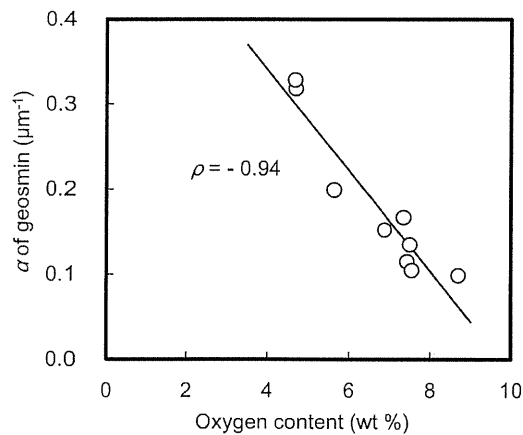


Fig. 3. Correlation between α of geosmin and oxygen content of carbon.

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

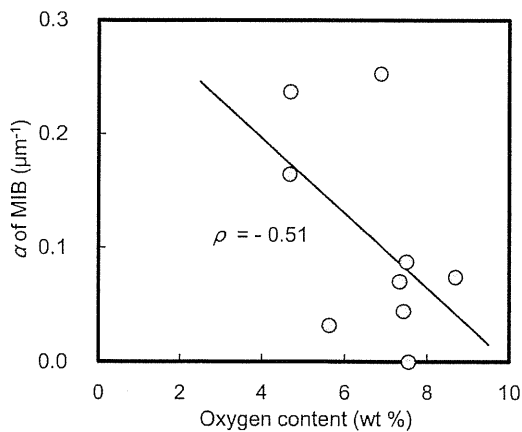


Fig. 4. Correlation between α of MIB and oxygen content of carbon.

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.

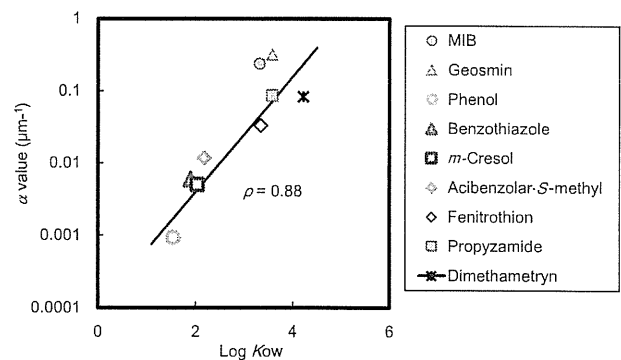


Fig. 5. Correlation between α and K_{OW} for various adsorbates on carbon A.

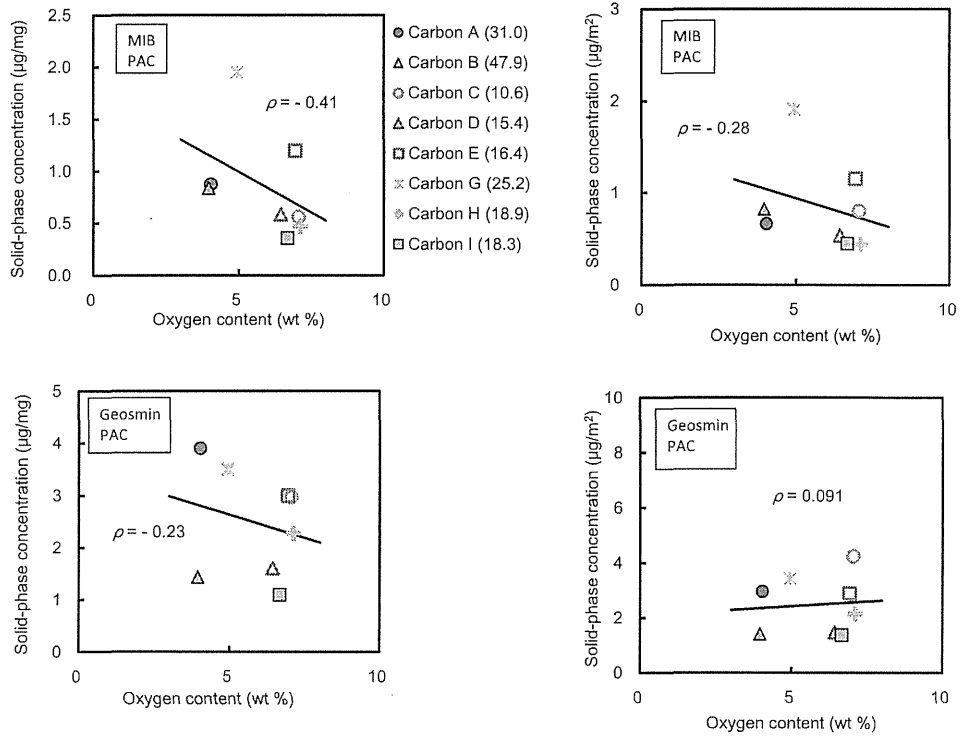


Fig. 6. Correlations between solid-phase adsorbate concentration for an equilibrium aqueous-phase concentration of 100 ng/L and PAC oxygen content for MIB (upper panels) and geosmin (lower panels). In the left panels, the values on the y-axis are adsorbate masses per unit mass of adsorbent, whereas in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

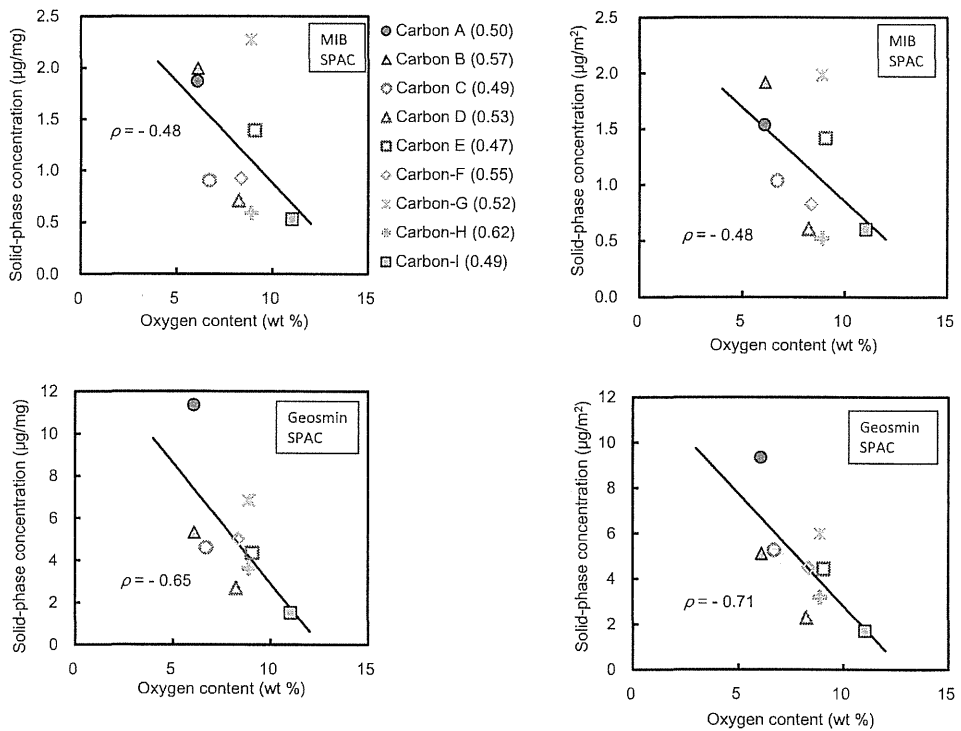


Fig. 7. Correlations between solid-phase adsorbate concentration for an equilibrium liquid-phase concentration of 100 ng/L and SPAC oxygen content for MIB (upper panels) and geosmin (lower panels). In the left panels, the values on the y-axis are adsorbate masses per unit mass of adsorbent, whereas in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