Passive sampling of polar and nonpolar halogenated pollutants in aquatic environments of Redcliffe, Australia

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Introduction

Monitoring of water quality is a key task for managers of environmental and public health since aqueous pollutants may pose a risk to human and environmental health. Routine methods commonly used for monitoring are based on the collection of one litre grab water samples. In general, these methods are often not sensitive enough to assess whether a risk exists and are limited to individual (sporadic) sampling events. The range of problems associated with this sampling strategy and method sensitivity has resulted in many attempts to develop alternative monitoring methods such as the collection and analysis of sediments and/or biota. However, predictions of water concentration from such methods are complicated by many factors related to the complexity of the biotic and abiotic environment (such as deposition rate and composition of sediments and mobility and metabolism in biota). Since Soedergren[1] demonstrated that hexane filled dialysis tubes can be used for monitoring organochlorines, there have been many innovative ideas developed as a response to the problems faced by other methods of environmental monitoring. Abiotic passive sampling techniques have become an exciting alternative for monitoring of aquatic and atmospheric pollutants. Due to work by Huckins et al.[2] and various others[3,4] the methods for quantitative prediction of nonpolar organic chemicals in water have been improved to a point where semipermeable membrane devices (SPMDs) can be considered a reliable quantitative monitoring tool for many pollutants. In addition, work since the mid 1990s has resulted in two separately developed passive samplers for polar organic chemicals, one developed by Kingston et al.[5] in the UK and, the second, the POCIS (polar organic chemical integrative sampler) developed at the United States Geological Survey[6]. Here we present monitoring data using passive sampling techniques for monitoring polar and nonpolar organic chemicals at five sites in Redcliffe, a semi-urban city near Brisbane. Furthermore, we provide data to assess the performance of the passive sampling technique and compare it with sporadic grab sampling results for polar organic chemicals.

Methods and Materials

Sampling sites: The study was carried out in the Redcliffe Shire which is situated in the South-east Queensland metropolitan area about 30 km north east of the Brisbane city centre. A total of five sampling sites were selected including three in a canal estate with a high level of boating activity, one in a tidal wetland receiving runoff from an industrial area, and finally a site in an essentially stagnant pond located in a residential area. This fifth site becomes a stream during major rain events.

Table 1: Sampling sites, description of the sites and major inputs identified that could influence the pollutant profiles

Location	Description	Expected inputs
Site 1	Outer part of a Canal estate, near the mouth into Deception Bay	Boats, residential runoff
Site 2	Central part of a Canal estate	Boats, residential runoff
Site 3	Upper part (least flushed) of a Canal estate	Boats, residential runoff
Site 4	Tidal drain in a mangrove near a light industrial area	Industrial activity, stormwater runoff
Site 5	Mostly stagnant pond in a residential park/floodway	Residential runoff and use of pesticides

Passive sampling deployment

Types of passive samplers used: Two types of passive sampling devices were used for the study to cover a wide range of potential chemicals of interest. The passive sampling techniques used included:

i.) Semipermeable membrane devices (SPMDs) for nonpolar chemicals such as organochlorine pesticides and PAHs. These were deployed in stainless steel devices that restrict the water flow and protect the devices.

ii.) Empore disk samplers (EDSs) These are comprised of a matrix of Teflon microfibrils bound to a highly efficient styrenedivinylbenzene reversed phase sulofonated copolymer sorbent. The disks were deployed in a teflon device developed by Kingston et al.5 for the sampling of polar and nonpolar organic chemicals. Samplers were deployed naked in the device without the use of an uptake limiting membrane, which facilitated a faster sampling rate.

Standard **SPMDs**: SPMDs were prepared from low density polyethylene (90 – 95 µm thickness) with a total area of 460 cm^2 and contained 1 mL of triolein (95 % purity, Sigma, Aldrich). The membranes were precleaned with hexane according to the instructions of Huckins *et al.*[7]. For in-situ calibration of the sampling rates two deuterated PAHs, anthracene and pyrene, were used as performance reference compounds (PRCs). This allowed a correction of the uptake rates in the sampler calculated from a clearance rate of the PRCs against values obtained in laboratory experiments. Once the SPMDs were prepared they were mounted into the stainless steel device and transported to and from the field in sealed acetone washed tin cans. Once retrieved, in the laboratory the SPMDs were cleaned according to the protocol of Huckins *et al.*[7]. The cleaned SPMDs were spiked with ten deuterated PAHs resealed and extracted by dialysis into hexane over two 24 hr periods. Sample purification included a clean-up using GPC Envirogel™ and silica gel. The purified extracts were concentrated to 50 µL and spiked with a deuterated recovery standard. The samples were analysed using GC-MS for a wide range of pesticides (> 80 individual chemicals) and PAHs. Detection limits were defined as three times field blank values or, where a compound could not be identified in the blanks, as three times the average noise peak area[8].

The **EDSs** 3M™ Empore™ Extraction Disks (C18), were conditioned using methanol followed by MilliQ water. The samplers, including field and laboratory blanks, were loaded with deuterated dimethylphthalate as a PRC. They were transferred to and sealed in the teflon housing, which also contained a small amount of MilliQ water to keep the matrix wet during transport and storage (Kingston *et al.*, 2000). No uptake limiting membrane was used for this study to facilitate faster sampling rates and to avoid selective uptake of analytes. EDSs were extracted into 5 mL of acetone (HPLC grade, Merck) for five minutes in an ultrasonic bath followed by 10 mL of a 50:50 mixture of trimethyl pentane and ethyl acetate in the ultrasonic bath.

The combined extracts were concentrated to 1 mL and 500 µL of methanol (HPLC grade, Merck) was added. This was filtered through a Millex 0.45 µm syringe driven filter unit, further reduced to 0.5 mL, made up to exactly 1 mL with MilliQ water and then transferred to vials for analysis. Polar sampler extracts were analysed by LC-MS/MS for eight priority herbicides: diuron, atrazine, simazine, tebuthiuron, flumeturon, hexazinone, ametryn, prometryn, as well as the breakdown products of atrazine, desethyl atrazine, and desisopropyl atrazine.
SPMDs and EDSs were deployed in replicates at all sites for two consecutive periods of 28 and 26 days starting late November 2003 (i.e. in the Australian summer period which reflects the wet season in Brisbane). However, for SPMDs only single samples were analysed since previous studies demonstrated that this technique provides usually very reproducible results[8].
In addition to the passive sampling, two one litre water samples were collected on five occasions over approximately two week intervals at each of the sites. These were analysed for polar organic chemicals. The samples were collected in solvent washed amber glass bottles and stored refrigerated until extraction. Extraction was carried out using the solid phase extraction technique (500 mg Oasis HLB extraction cartridges, Waters). The cartridges were conditioned with 5 mL of MeOH followed by 5 mL of MilliQ water. The samples were eluted into 10 mL of methanol reduced to 1 mL and analysed for herbicides using LC-MS/MS as described above for EDSs.
Concentrations of chemicals in the water were calculated from the passive sampling data using different models and calibration data obtained in different laboratories. For SPMDs the calculations were carried out using calibration data provided by Huckins et al.[7]. For EDSs these results represent one of our first studies with these samplers. Calibration studies carried out parallel to this study showed that for chemicals such as diuron and atrazine the EDS to water partition coefficients are sufficiently low for naked EDSs to deviate from linear kinetics after 5 - 8 days and the samplers attain equilibrium in four weeks. Hence, for this study we based the calculation of the water concentration on sampler–water partition coefficients that were determined in the laboratory according to $K_{sw} = C_s/C_w$ where K_{sw} is based on the volume of sorbent in the SDB-RPS Empore disk. The K_{sw} for the herbicides were obtained in a separate study (Stephens *et al.* submitted for publication and unpublished data) with $\log_{10} K_{sw}$ of 4.43; 4.58 and 4.60 for diuron, simazine and atrazine respectively.

Results and Discussion

Atrazine, diuron and simazine were detectable at all five sites using both grab water samples and the polar passive samplers. Diuron concentrations in the water based on passive sampling results, ranged from 33 ng/L in the first sampling period (November/December 2003) at Site 5, to 240 ng/L in the second sampling period at Site 3. The reproducibility of the results was very good in samples from Sites 1-3 with coefficients of variation < 30 %. However, a lower reproducibility of the technique was found at Sites 4 and 5. Site 5 was a stagnant pond and Site 4 a drain where the water level may have dropped so low that the samplers were sitting in sediment, both these site specific factors may have affected the results (Table 2).
Table 2 – Predicted concentrations of herbicides in the water from passive sampling results (based on an equilibrium model). * found only in one of three replicants.

Site	Period	Atrazine [ng/L]	Simazine [ng/L]	Diuron [ng/L]
1	1	1.4 ± 0.34	9.9 ± 2.7	140± 11
	2	1.0 ± 0.16	7.7 ± 0.73	120 ± 8.3
2	1	1.0 ± 0.01	7.5 ± 0.95	150 ± 12
	2	0.79 ± 0.11	7.1 ± 0.95	110 ± 12
3	1	0.92 ± 0.01	9.4 ± 0.94	240 ± 5
	2	0.81 ± 0.26	7.5 ± 2.3	190 ± 58
4	1	0.12 *	27 ± 5.9	45 ± 15
	2	-	-	-
5	1	7.3 ± 5.8	12 ± 7.9	9.8 ± 6.1
	2	0.40 ± 0.11	14 ± 7.8	33 ± 17

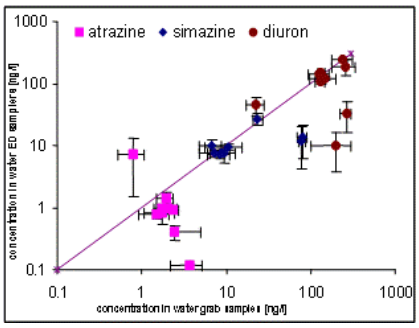

Figure 1: Comparison of predicted concentration of herbicides from passive sampling data with data from grab sampling.

A comparison between the active and the passive sampling results showed good agreement of levels at Sites 1-3 and Site 4. For example, the predicted mean water concentrations obtained from passive sampling at these sites were generally consistently within the data range observed from the five grab sampling events during the two deployment periods. For Site 5, the stagnant pond, simazine and diuron concentrations calculated from passive sampling data appeared to be much lower than those observed in grab water samples. In contrast, the passive samplers predicted atrazine concentrations that were higher than those observed in grab water samples. The underestimation of the concentration of diuron and simazine with the passive samplers suggests the uptake in the samplers may have been slower at this site and thus had not reached equilibrium within the exposure period. For atrazine the grab sampling results were very variable and mostly below the limit of detection (LOD), however there were values up to those predicted from the passive sampling results. Hence, for atrazine the grab sampling results are difficult to interpret.

Monitoring of nonpolar organochlorines was carried out with semipermeable membrane devices. The measured concentrations range from 0.0074 ng/l (cis-chlordane Period 1 at Site 1) to 7.8 ng/l (dieldrin Period 2 at Site 5). Overall, the largest number and concentrations of analytes (including a variety of chemicals that have been banned for use over recent decades, such as dieldrin, DDT and chlordanes) were detected at Site 5, the stagnant freshwater pond in the middle of Redcliffe (Figure 2). This is likely due to the longer retention of chemicals in the pond. Notably, this was also the only site where we were able to detect degradation products of atrazine.

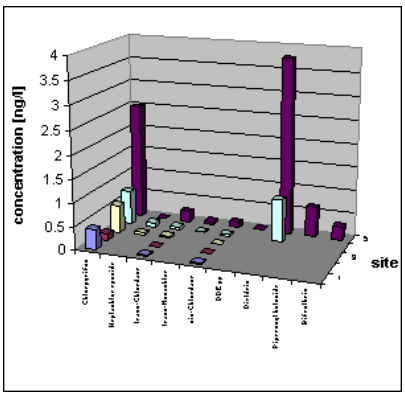

Figure 2a - Concentration of pesticides during period 1

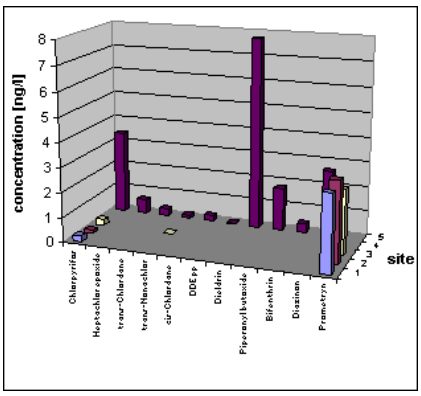

Figure 2b - Concentration of pesticides during period 2

Acknowledgement

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