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► **To cite this version:**

Catherine Berho, Anne Togola, Charlotte Coureau, Jean Philippe Ghestem, Laurence Amalric. Applicability of polar organic compound integrative samplers for monitoring pesticides in groundwater. Environmental Science and Pollution Research, 2013, 20 (8), pp.5220-5228. 10.1007/s11356-013-1508-1. hal-00933450

HAL Id: hal-00933450

<https://brgm.hal.science/hal-00933450>

Submitted on 20 Jan 2014

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Applicability of Polar Organic Compounds Integrative Samplers for monitoring pesticides in groundwater

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Abstract

Polar Organic Chemical Integrative Samplers (POCIS) for the monitoring of polar pesticides in groundwater were tested on two sites in order to evaluate their applicability by comparison with the spot-sampling approach. This preliminary study shows that, as in surface water, POCIS is a useful tool, especially for the screening of substances at low concentration levels that are not detected by laboratory analysis of spot samples. For quantitative results, a rough estimation is obtained. The challenge is now to define the required water-flow conditions for a relevant quantification of pesticides in groundwater and to establish more representative sampling rates for groundwater.

Keywords: groundwater; pesticide; monitoring; passive sampling; POCIS; screening;

Abbreviations

Polar organic chemical integrative sampler	POCIS
Time weighted average	TWA
Desethylatrazine	DEA
Desisopropylatrazine	DIA
Desethylterbuthylazine	DET

Ground Water Directive	GWD
Solid phase extraction	SPE
Polyethersulfone	PES
Ultra performance liquid chromatography	UPLC
Relative standard deviation	RSD
Multiple Reaction Monitoring	MRM

Introduction

Groundwater represents up to 97% of the freshwater resources in the European Union (EU). At the European level, groundwater protection is covered by several directives including the (GWD) 2006/118/EC on the protection of groundwater against chemical pollution and deterioration (EC, 2006). In this directive, groundwater monitoring is a key point in the process of evaluating the quantitative and chemical status of European groundwater resources. The most common approach of water monitoring based on spot sampling followed by laboratory analysis is validated and accepted for regulatory purposes (Allan et al. 2006). To provide a representative sample of the aquifer, sampling usually involves purging the well beforehand, though with minimal disturbance to the groundwater flow. Regulatory guidelines generally recommend that a minimum of three to five well volumes of water should be purged before the physico-chemical parameters have sufficiently stabilized to allow sampling (MDBC, 2007; Sundaram et al. 2009). This classic sampling approach has well known drawbacks; subsequent pumping may disturb contaminant distribution between the whole aquifer and groundwater leading to a non-representative sample due to dilution or increase in the real contaminant concentrations (Bopp et al. 2005; Yeskis and Zavala, 2002; Puls, Robert and Barcelona 1996), vertical mixing that can hide a potential stratification of contaminants (McDonald and Smith 2009) or the introduction of air that can volatilize pollutant compounds (Parker 1994). In addition, spot sampling only provides a snapshot of the contamination and is not sufficient for water matrices subjected to temporal variations. Increasing the sampling frequency or automatic sampling could be a solution, but this would be laborious and expensive (Vrana et al. 2005b).

To face these limitations, passive sampling techniques seem to be a good alternative, and have been tested for monitoring contaminants in aquatic environments (Stuer-Lauridsen, 2005; Kot-Wasik et al. 2007; Söderström et al. 2009; Greenwood et al. 2007). The different chemical potentials of the analytes between the two media result in an *in situ* enrichment and isolation of analytes in the receiving phase and avoid the well-known drawbacks of classical sampling (Zabiegala et al. 2010). Kinetic and equilibrium regimes can be distinguished. In the case of equilibrium passive sampling, there is thermodynamic equilibrium between the water and the receiving phase. With kinetic or integrative passive samplers, the rate of mass transfer to the receiving phase is linearly proportional to the difference in chemical activity of the contaminant between the water phase and the receiving phase. Their main advantages of the latter method are: 1) The preconcentration of contaminants increases the capability of detecting trace concentrations; 2) When the proportionality constant or sampling rate is known, the Time Weighted Average (TWA) concentration of a pollutant in the water phase can be calculated, which corresponds to the mean concentration in the medium during passive sampling. This allows the detection of pollutants from episodic events, generally not taken into account with the spot-sampling approach (Vrana et al. 2005b). However, the main drawback of passive samplers is the difficulty of the calibration. Indeed, environmental conditions (water flow, temperature, pH, biofouling) can affect contaminant uptake (Macleod et al., 2007; Alvarez et al., 2004; Booj et al., 2003; Huckins et al., 1999). Unlike for surface waters and effluents, very few publications deal with the use of integrative passive samplers in groundwater. However, passive samplers neither need pumping, nor disturb the groundwater. Most publications deal with the monitoring of industrial contaminants, such as polycyclic aromatic hydrocarbons (PAHs) and volatile aromatic compounds, by using ceramic dosimeters or semi-permeable membrane devices (SPMD) (Bopp et al. 2005; Martin et al. 2003; Vrana et al. 2005a; Kingston et al. 2000; Bidwell et al. 2010). These publications show that such integrative passive samplers are suitable tools for monitoring contaminant concentrations in water, even if the limitation of the *in situ* extraction potential of the SPMD by groundwater flow is mentioned (Vrana et al. 2005a; Kingston et al. 2000). Concerning passive sampling for polar organic compounds in groundwater, only two publications dealing with the use of POCIS for screening (qualitative information) of polar contaminants in creeks and shallow groundwater were found (Dougherty et al. 2010; Bidwell et al. 2010).

Pesticides are a group of compounds of great concern as they belong to the pollutants that require quality standards for defining the chemical status of groundwater under the GWD. The GWD requires the definition of both the levels of pesticide contamination in groundwater, and the trends of such pesticide concentrations. To achieve this goal, monitoring is generally based on a low measurement frequency (1 to 4 analyses per year), even though some publications pointed out a monthly variability of pesticides in groundwater (Baran et al. 2008; Morvan et al. 2006; Choquette and Kroening 2009) that cannot be detected by such infrequent spot sampling. Passive sampling would be particularly relevant for considering the short-term temporal variability and vertical distribution of pesticides.

In this context, the aim of this work was to test the applicability of Polar Organic Integrative Samplers (POCIS) for detecting and quantifying polar pesticides in groundwater. POCIS is the main passive sampler used for monitoring polar pesticides (Mills et al. 2011). It was tested on two sites in an observation well, in order to evaluate its applicability for monitoring pesticides in groundwater compared to the spot-sampling approach. Qualitative information obtained with POCIS is presented hereafter, as well as quantitative data based on the calculation of the TWA concentrations.

Material and methods

Analytical standards for pesticides (purity >98%) were purchased from RESTEK (Lisses, France), and HPLC-grade acetonitrile and methanol were obtained from Fischer Scientific SAS (Ilkirch, France). Deuterated labeled compounds, simazine-d10 (purity >99%) and atrazine-d5 (97.5%) were obtained from CDN Isotopes (CIL-Cluzeau Sainte-Foy-La Grande, France). Acetonitrile and methanol (HPLC grade) were purchased from Fisher Chemical and formic acid was from Avantor (Deventer, the Netherlands).

Oasis™ HLB (divinylbenzene/*N*-vinylpyrrolidone copolymer) extraction cartridges (500 mg, 6cc, 60 µm) were purchased from Waters Corporation (Guyancourt, France). Empty polypropylene SPE Tubes with polyethylene frits were supplied by Supelco (Saint-Quentin Fallavier, France).

A different POCIS geometry than is normally used was chosen due to the limitation of sampler size by the borehole diameter. POCIS pharmaceuticals in groundwater configuration (29-cm long, 5-cm diameter, surface area 95 cm²) were purchased from Exposmeter (Tavelsjö, Sweden). The sorbent mass (OASIS™ HLB-divinylbenzene/*N*-vinylpyrrolidone copolymer) is about 450 mg; the ratio between surface and mass sorbent in the POCIS is of the same order as for surface water configuration (approximately 200 cm²/g).

Extraction and Analysis of pesticides from water samples

Polar herbicides were extracted from 1 litre water samples by solid-phase extraction Oasis™ HLB cartridges at neutral pH using the autotrace SPE workstation (Caliper LifeSciences, Villepinte, France). Cartridges were preconditioned successively with 5 mL acetonitrile, 5 mL methanol and 5 mL of ultrapure water at 5ml/min. Before extraction, water samples were spiked with a surrogate (atrazine-d5) at 100 ng/L which allows checking the extraction step by verifying the extraction yield of the surrogate (between 87 and 97% for all samples). The samples were passed through the cartridges under vacuum at a flow rate of 10 mL/min. Before elution, cartridges were dried under vacuum for 1 hour. Elution was done with 2*4 mL of acetonitrile at a flow rate of 3 mL/min. The extracts obtained were evaporated to 1 mL at a flow rate of 3 mL/min in a nitrogen stream and transferred into injection vials. Simazine-d10 (50 µl in acetonitrile) was added as an internal standard (100 ng/mL in extract) for quantification.

A total of 25 polar herbicides that belong to triazine, phenylurea and substituted anilide chemical groups (Acetochlore, Alachlore, Ametryne, Atrazine, Chlortoluron, Desethylatrazine, Desethylterbuthylazine, Desisopropylatrazine, Cyanazine, Desmetryne, Diuron, Hexazinon, Isoproturon, desmethyl Isoproturon, didesmethyl Isoproturon, Linuron, Metalachlore, Metolachlore, Prometryne, Propazine, Propyzamide, Sebuthylazine, Simazine, Terbuthylazine,

Terbutryne) was quantified with a UPLC-MS/MS Quattro Premier XE (Waters Instruments) in Multiple Reaction Monitoring mode using electrospray ionization (ESI +) and controlled by MassLynx software. The column used was a UPLC-BEH-C18 column (1.7 μm ; 2.1 mm x 150 mm; Waters). The mobile phase was composed of solvent A (0.05% formic acid in water) and solvent B (0.05% formic acid in acetonitrile) at a constant flow of 0.4 mL/min. The gradient was programmed to increase the amount of B from 0% to 100% in 7.5 min, with stabilization for 1.5 min, before return to initial conditions in 0.3 min for 5.30 min. Matrix effect is considered as negligible due to the small injected volume (2 μL) and the low organic-matter content in the extracts of groundwater sample. Indeed, in the frame of the method validation, the measurements of 5 different spiked natural waters at three levels of concentrations (50, 100, 150 ng/L) confirms that there is no matrix effect.

This analytical method dedicated to the measurement of pesticides in water samples is accredited according to the ISO 17025 (2005) standard by COFRAC (French accreditation organization). Validation was based on the NFT 90-210 (2009) French standard, which itself is based on the reference standards ISO 5725 Part 1, 2, 3 (1994) and ISO/TR 13530 (1997).

Method validation was based on an accuracy profile on 5 days using two replicates per day of spring water samples spiked with a mixture of all analytes at 3 concentration levels (5, 50, 100 $\text{ng}\cdot\text{L}^{-1}$). These tests defined the extraction yield, the limit of quantification, the intermediate reliability and the measurement uncertainty. The results for each concentration level were interpreted to verify the precision and accuracy of the method in relation to an acceptable maximum deviation around each reference value. The uncertainty was calculated by taking into account the intermediate reliability and the uncertainty on the 3 doping levels. The uncertainty was raised by a factor $k=2$ and the value rounded up to the next five to comply with the XPT 90-220 French Standard (2003). The extraction yield was between 75 and 83% depending on substances. The limit of quantification was validated according to NFT 90-210 (2009) French standard at 5 ng/L for all substances except for diuron for which it was 10 ng/L. The uncertainty ($k=2$) was between 20 and 40% depending on the substances.

Specificity was also checked by the analysis of 5 other water samples (spring waters, surface waters, groundwaters) spiked at several levels of concentration (limit of quantification, 50, 100, 150 ng/L) in presence of non-targeted pesticides substances over 4 different days and with different calibrations.

POCIS extraction and analysis

After environmental exposure, each POCIS sampler was rinsed with ultrapure water to remove any material adhering to the surface membrane before disassembly. The sorbent powder was carefully transferred into an empty polyethylene cartridge of 3 mL polyethylene frit, and the membranes were detached and rinsed with ultrapure water to recover all sorbent. POCIS extraction and analysis is based on the validated protocol described above for water samples except that elution is done with methanol (instead of acetonitrile) as indicated in the publication of Mazzella et al. (2007). The non-influence of the elution solvent was verified by the analysis of a spiked spring water solution containing all pesticides at 1000 ng/L each after extraction with the both solvents independently. The differences observed between results are from 1 to 22% depending on substances, which is below the uncertainty of the analytical method.

The cartridge was dried under vacuum by using a Visiprep SPE Manifold (Supelco) for 1 hour and eluted using 2*4 mL of methanol. The extracts obtained were finally evaporated to 0.5 mL under a nitrogen stream and transferred into injection vials. Simazine-d10 (25 µl) was added as an internal standard (100 ng/mL in extract). Cartridges were placed in a dessicator during 12 hours for drying and the mass of sorbent was measured by gravimetry for each POCIS.

Calculation of the Time Weighted Average (TWA) concentration

The TWA concentration (C_w) was calculated according equation (1):

$$C_w = m / R_s t \quad (1)$$

where m is the accumulated mass (ng/g POCIS); R_s is the sampling rate (L/day/g POCIS) and t is the duration of deployment (days).

In order to be close to groundwater flow conditions, sampling rates from laboratory calibrations in quiescent conditions using a static renewal scheme were chosen from the literature, though few data are available. R_s values were found for atrazine and diuron (Alvarez et al. 2004; Alvarez et al. 2007). For DEA, metolachlor and simazine, the only data found were obtained from seawater (Hernando et al., 2005). We can suppose that salinity has no effect on neutral substances, such as triazines and metolachlor, comparing the sampling rates in distilled water and seawater for atrazine, under quiescent conditions (0.05 L/day and 0.053 L/day), or under stirred conditions (0.24 L/day (Mazzella et al. 2010) and 0.214 L/day (Martinez Bueno et al. 2009)).

We therefore chose to use quiescent sampling rates obtained on seawater for DEA simazine and metolachlor, for a rough estimation of TWA concentrations. Table 1 presents the sampling rates used to estimate TWA concentrations.

Environmental field deployment

POCIS were tested on two sites that were chosen because of the well-documented presence of polar pesticides in the groundwater: historical data were found in ADES, the French public national bank of groundwater data, available at www.adeseaufrance.fr.

Site 1 is a drinking-water-supply site located near Paris that was closed due to the presence of pollutants at low concentrations. The observation well (6 m deep) is located in an alluvial aquifer. Four successive sampling campaigns of 17 days, 14 days, 21 days and 13 days duration, respectively, were organized from July to November 2011. Standard sampling was done with a twister pump at 3 m depth in the water column before and after purging (3 times the well volume), associated with physico-chemical parameter measurements in order to check the representativeness of the water in the well at the introduction and at the retrieval of the passive samplers. The POCIS were deployed in duplicate on a polyethylene chain at two depths in the

water column (2 m and 4.5 m). A Field blank was deployed at the air at the beginning and the end of each campaign during the deployment and the retrieval of POCIS on the chain.

Site 2 is located near Troyes (France), in an alluvial aquifer upstream from a well field. It is 18 m deep with a screened interval from 6 to 18 m depth. Historic data for the site 2 showed that the pesticide concentrations in the water are stable. In order to confirm the data, pesticide concentrations in groundwater were measured twice a day during five days before the passive-sampling field trial: sampling was done with a submersible pump at 12 m depth after purging (3 times the well volume and stabilization of physico-chemical parameters). After that, two successive passive-sampling campaigns of 7 days duration were organized. POCIS were deployed in duplicates on a polyethylene chain at 10 and 15 m depth in the screened interval.

Results

Pesticide concentrations in groundwater samples

Representativeness of water in the well before purging (site 1)

Figure 1 shows pesticide concentrations in groundwater samples before and after purging over the four campaigns in Site 1. The results show that four polar pesticides were quantified at low concentration levels (<100 ng/L) for the 25 targeted substances. Mean pesticide concentrations for the four campaigns before and after purging were similar and water in the well was thus representative of the aquifer. These results were confirmed by the physico-chemical parameters before and after purging for the four campaigns: no significant impact of purging was observed on the physico-chemical parameters (RSD <21% regardless of the parameter), which confirms the representativeness of the water in the observation well.

Variation of pesticide concentrations in groundwater

Figure 2 shows the variations in pesticide concentrations in groundwater after purging during the four campaigns (C1, C2, C3, and C4) in site 1. Slight variations in concentrations of the spot samples were observed over the four campaigns.

For the site 2, analysis of groundwater samples as indicated in the section “Environmental field deployment” showed that the pesticide concentrations in the water were stable. 6 pesticides among the 25 substances were quantified: atrazine (407 ng/L), desethylatrazine (385 ng/L), desisopropylatrazine (67 ng/L), desethylterbutylazine (35 ng/L), simazine (104 ng/L) and terbutylazine (23 ng/L). Regardless of the pesticide, the RSD was low and in the same range as the analytical variability (4%).

Pesticide quantity (ng/g) in POCIS

Reproducibility of the accumulation and screening of compounds

Figure 3 presents the mean accumulated mass (ng/g POCIS) per day in order to smooth the results for the duration of the four campaigns which were not exactly of the same time duration (site 1). The quantity of pesticides accumulated on POCIS was not the same for all campaigns, whereas the pesticide concentrations in water were relatively stable (Fig. 3). Accumulation was not reproducible for all campaigns: C1 and C4 present similar results with accumulations of about 5, 12, 1 and 2.5 ng/g of atrazine, desethylatrazine, desisopropylatrazine and simazine, respectively. For C2 and C3, less accumulation was noted at about 1.2, 2.5 and 0.5 ng/g for atrazine, desethylatrazine and desisopropylatazine respectively. Variations in water flow between the four campaigns may have been responsible for the differences observed in terms of accumulation. Such variations were probably caused by tests of the water-supply unit near the observation well which modified water flow in the study well but for which the well-field operator could not say exactly when they took place.

Figures 4A and 4B present the mean pesticide quantities found in POCIS (ng.g⁻¹) during the two campaigns on site 2. Accumulation was from 2 ng/g to 1300 ng/g depending on the substances. For the campaign C1, the mean accumulation was higher than for campaign C2: the ratio

between the two accumulations was from 1.2 to 1.8. The same pesticides were detected as those found in the water samples i.e. atrazine, desethylatrazine, desethylterbutylazine, desisopropylatrazine, simazine and terbuthylazine. In addition, metolachlore (2 ng/g POCIS), propazine (about 100 ng/g POCIS), hexazinon (3 ng/g POCIS) and diuron (30 ng/g POCIS), not found in water samples, were also detected by POCIS. These results highlight the fact that POCIS is useful for the screening for pesticides at very low concentrations in groundwater.

Time Weighted Average (TWA) pesticide concentrations calculated from POCIS

TWA concentrations were calculated for each campaign. Figure 5 compares the TWA concentrations with those measured in the groundwater in which POCIS were deployed (mean between the concentration after the initial purging and the concentration before purging at the end of the campaign). Differences between TWA concentrations and spot samples concentrations were from 1 to 4 (campaign C1), 0.5 to 1.2 (campaign 4) and much higher i.e 3 to 9 for campaigns C2 and C3.

Figures 6A 6B 6C compare the TWA concentrations and the spot-sampling pesticide concentration in site 2. TWA concentrations mirror the pesticide concentrations measured in water. For atrazine and simazine in the campaign 2, the TWA concentrations are in good agreement with concentrations in water. For DEA, the TWA concentrations lead to an overestimation of pesticides concentrations in water (factor 2 to 4) depending on the campaign.

The TWA concentration in diuron was estimated at 60 ng/L although this compound was not detected by classical analysis on water samples (limit of quantification of 10 ng/L). This might be due to variations of low concentrations in diuron over time.

Discussion

The use of passive samplers in groundwater requires that the water in the well is representative of that in the aquifer (ITRC, 2007). In our study, the representativeness of water in the well was thus checked in (Site 1). Other studies have already shown that water within the screened section of a

well are representative of adjacent groundwater (Robin and Gillham 1987; Powell and Puls 1993; Yeskis and Zavala 2002) and that purging is not necessary. This indicates that one of the main requirements for the applicability of POCIS in groundwater is fulfilled.

Detection of pesticides on POCIS shows that, in spite a low water flow by comparison with surface water, there is an effective accumulation of compounds in POCIS, a further indication that screening applications through piezometers are feasible.

However, the accumulation of pesticides on POCIS was not exactly the same from one campaign to the next whereas little variation of the concentrations in water samples was observed. This may be explained by variations in the water flow throughout the campaigns period. This difficulty has to be overcome in the use of POCIS for obtaining quantitative information and any outside influences such as pumping near the study site that might modify the water in the observation well have to be identified and controlled.

Sampling rates from the literature provided a rough estimate of pesticide concentrations in groundwater for the two test sites depending on the campaigns and the substances. However, to obtain quantitative information with POCIS, we need further research for defining representative sampling rates in groundwater. The use of Performance Reference Compounds (PRC, deuterated contaminants of interest) could be a solution when evaluating environmental conditions; indeed, the PRC approach is widely used for surface waters in order to correct the laboratory sampling rates in the case of passive samplers for middle-polar and apolar organic compounds (Petty et al. 2000; Huckins et al. 2002; Mazzella et al. 2010). For POCIS, the effectiveness of PRC has not yet been clearly demonstrated (Mills et al. 2011), although some studies used deuterated (d5) deisopropylatrazine as PRC in POCIS (Mazzella et al. 2010). Nevertheless, the use of deuterated compounds in groundwater—which is likely to be used as a drinking water supply—seems to be difficult to defend, even at low concentrations.

It is thus clear that, in addition to investigating the impact of reduced water flow, further specific studies are needed for studying the wide-spread applicability of POCIS:

- the development of calibration systems that are more representative for groundwater for estimating the range of sampling rates that is representative of groundwater conditions; Indeed, the study of water circulation and the impact of low water flow on the uptake of compounds is necessary.
- In situ calibration studies on reference sites for which the pesticide concentrations are known and stable (accumulation curve with time of deployment) or the use of in situ calibrations tools for groundwater based on the principle of the passive flow monitor for surface waters developed by O' Brien et al., 2009
- Sampling with a discrete-interval sampler at the same depth of deployment as the POCIS, could be performed for checking the quality of the water sampled by the POCIS. Indeed, if sampling rate is higher than daily turnover of the groundwater volume in the sampled borehole, POCIS will not provide a representative sample
- Field tests on several types of groundwater, incorporating groundwater-flow measurements are needed for a more precise evaluation of the applicability of POCIS.

Conclusions

We present the first results of applying POCIS for monitoring pesticides in groundwater from piezometers. Our results demonstrate that POCIS detect compounds and could be specifically used in the screening of substances at low concentration levels which are not detected by the usual techniques of spot sampling followed by laboratory analysis. Further research is needed for obtaining quantitative data and defining the required conditions in terms of optimum water flow for field applications. In a second step, POCIS could be tested on groundwater sites which present temporal variations in concentrations for studying its integrative capacity. In addition, it should be deployed at different depths for assessing the vertical distribution and/or stratification of pollutants in a well, provided no vertical flow within the well mix the water column.

Acknowledgements

We acknowledge financial support from ONEMA (AQUAREF) and the Scientific Division of BRGM. We also thank the BRGM technicians who carried out the field sampling and analysis. We also thank Marinus KLUIJVER for the English corrections of this publication.

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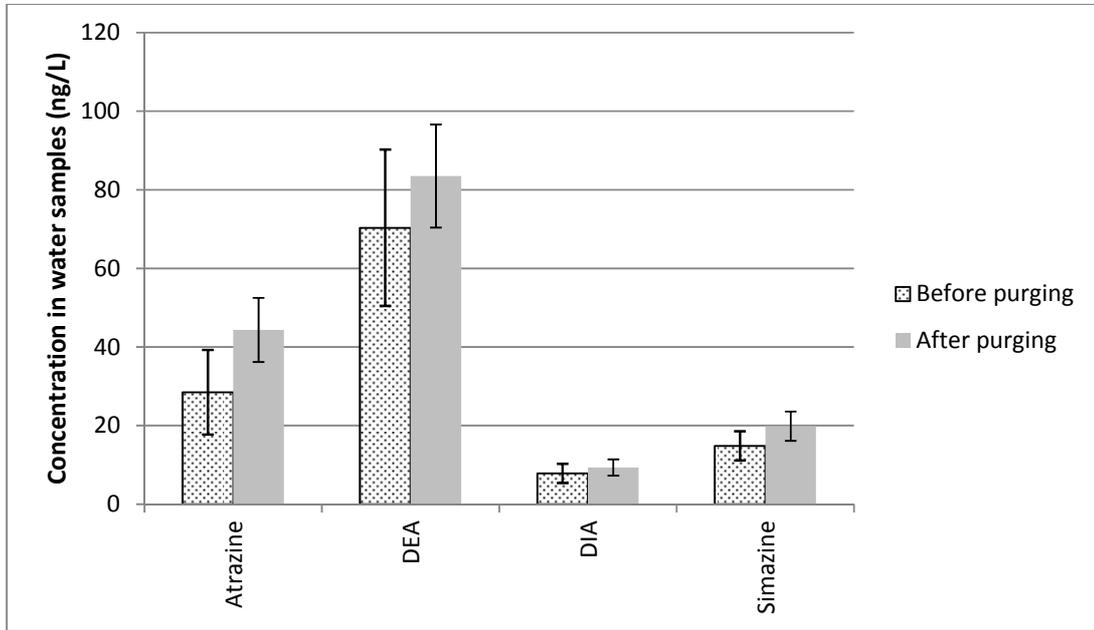


Figure 1: Mean pesticide concentration in spot water samples (n=6) over the four campaigns before and after purging on Site 1.

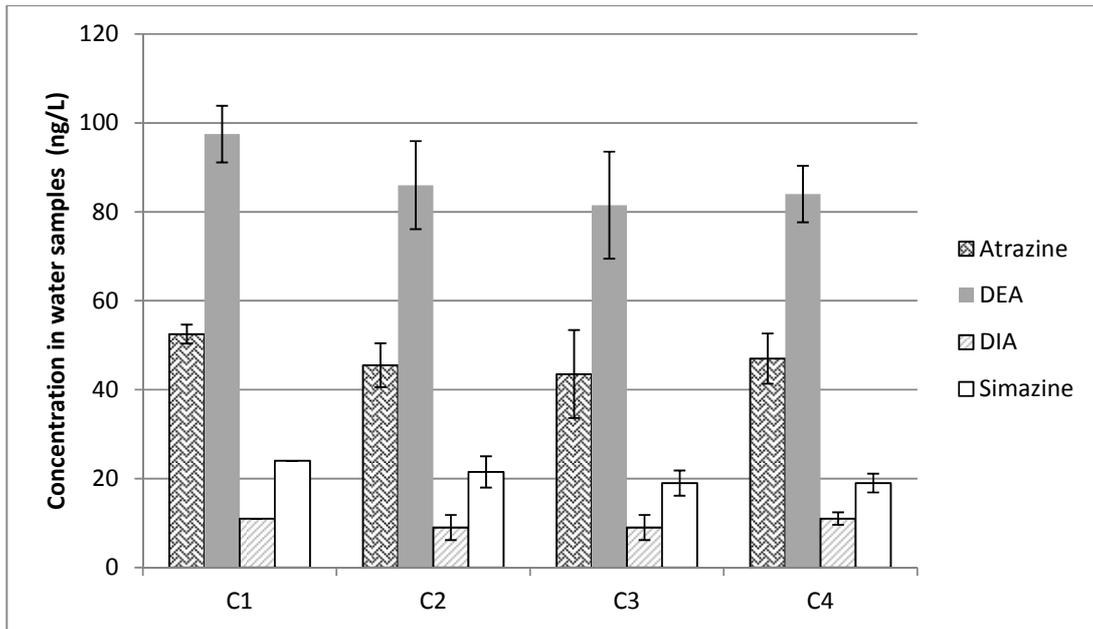


Figure 2: Mean pesticide concentrations in spot water samples after purging (n=2) during each campaign in Site 1. Errors bars represent standard deviation.

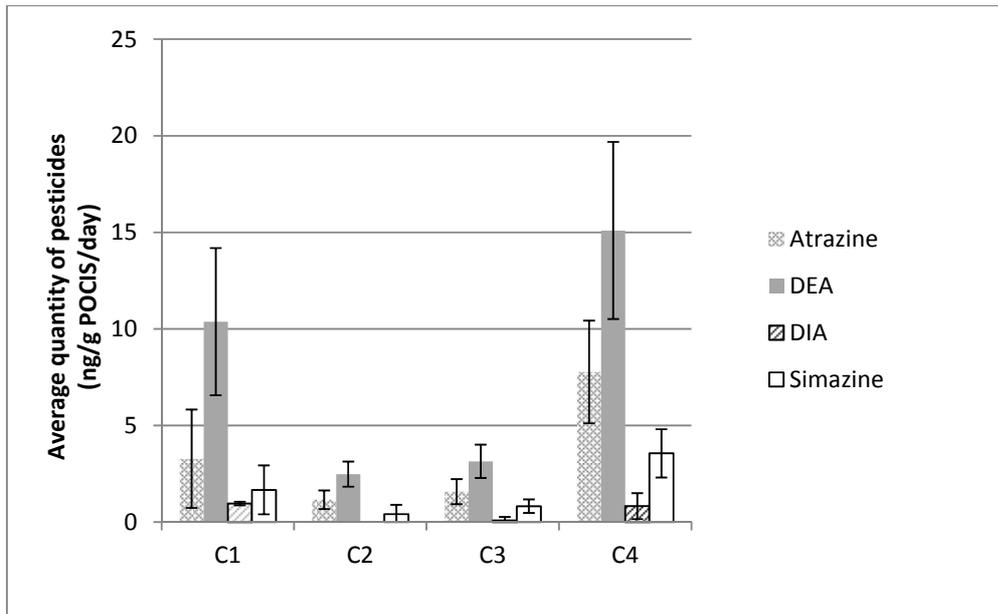
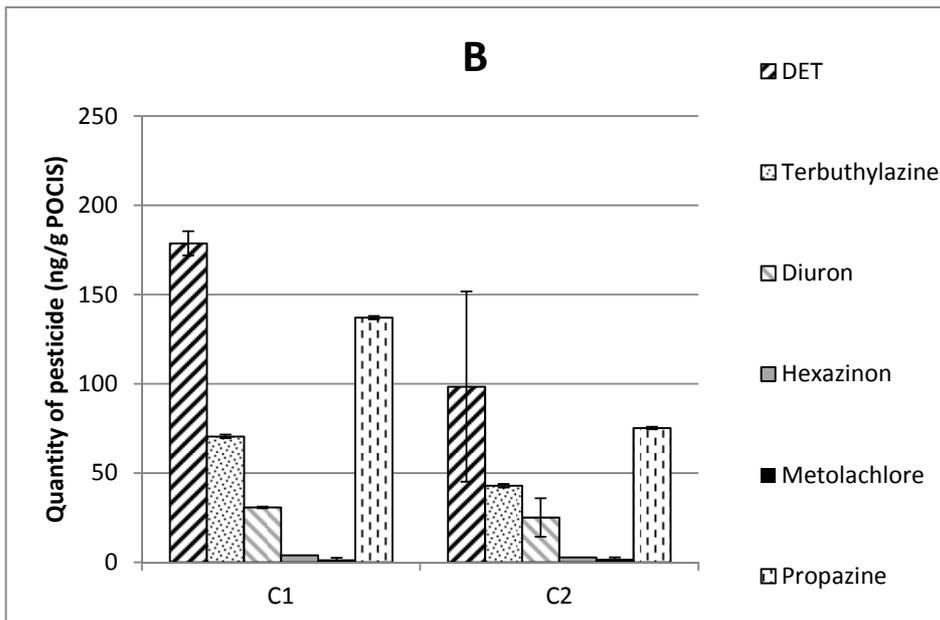
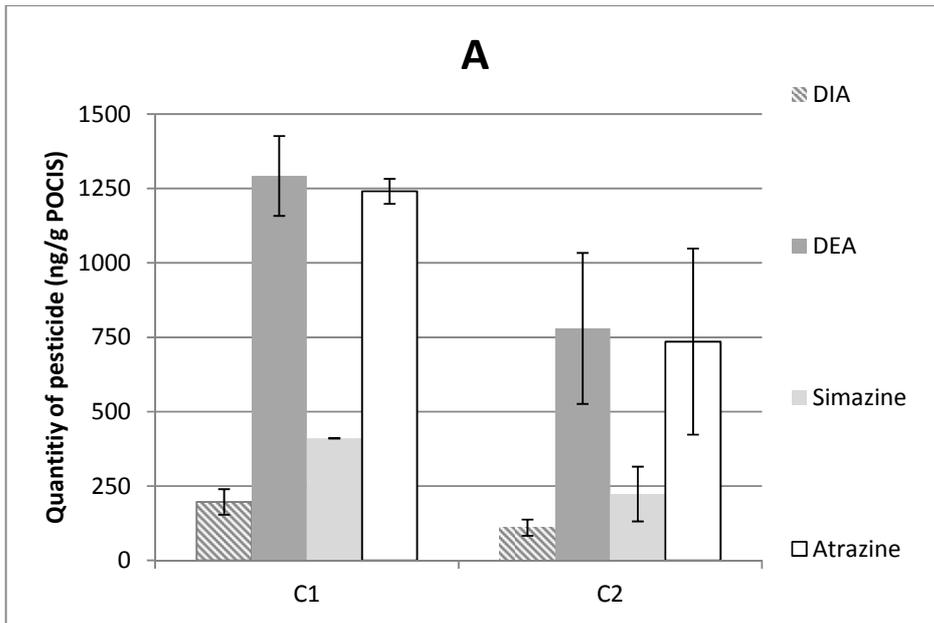


Figure 3: Average quantity of pesticide accumulated per day during each campaign in site 1 (n=4). Errors bars represent standard deviation.



Figures 4A and 4B: Quantity of pesticides accumulated on POCIS in site 2 during each campaign (n=2). Errors bars represent standard deviation.

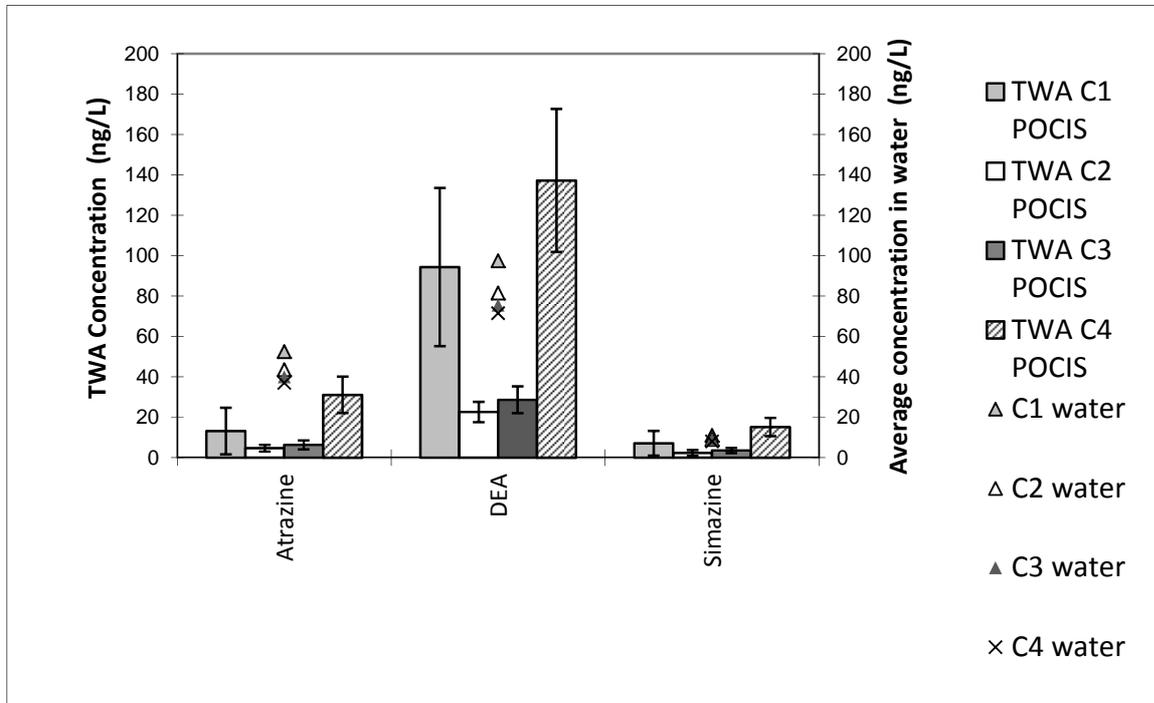
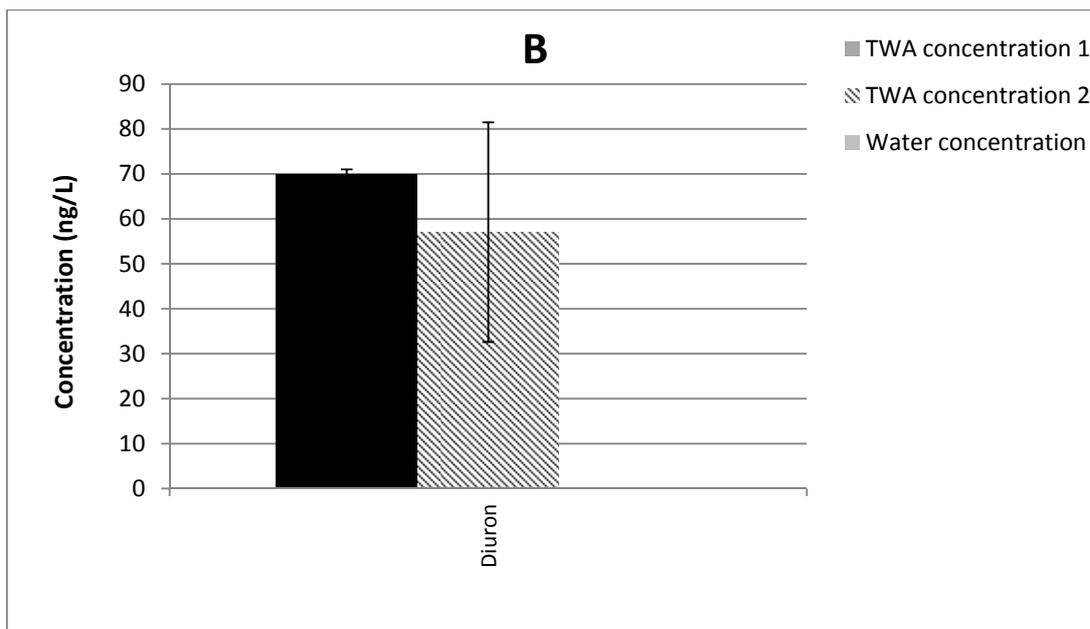
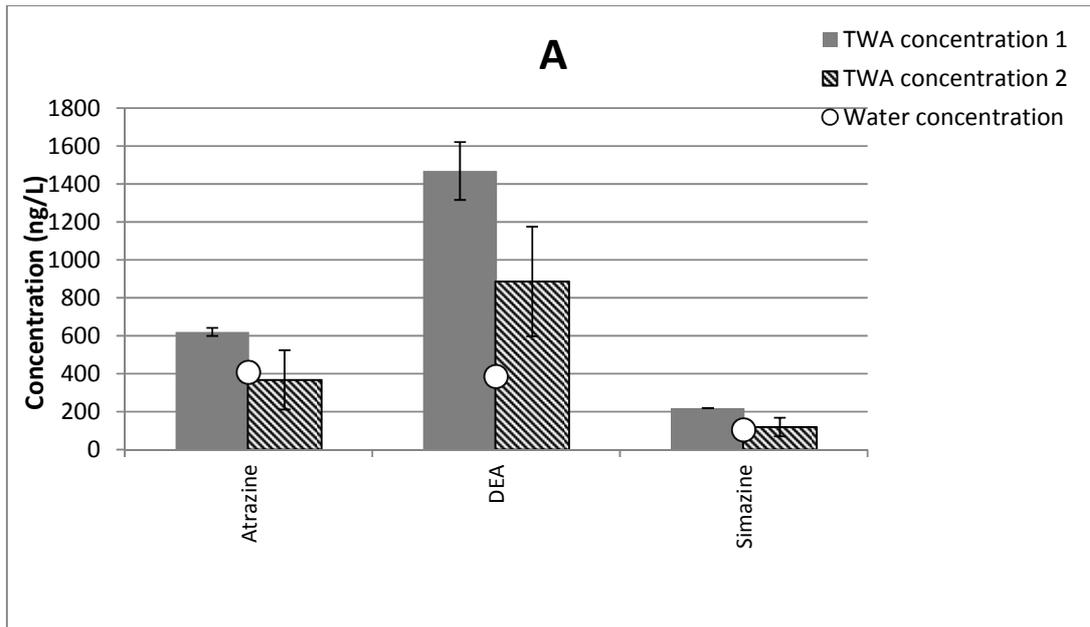
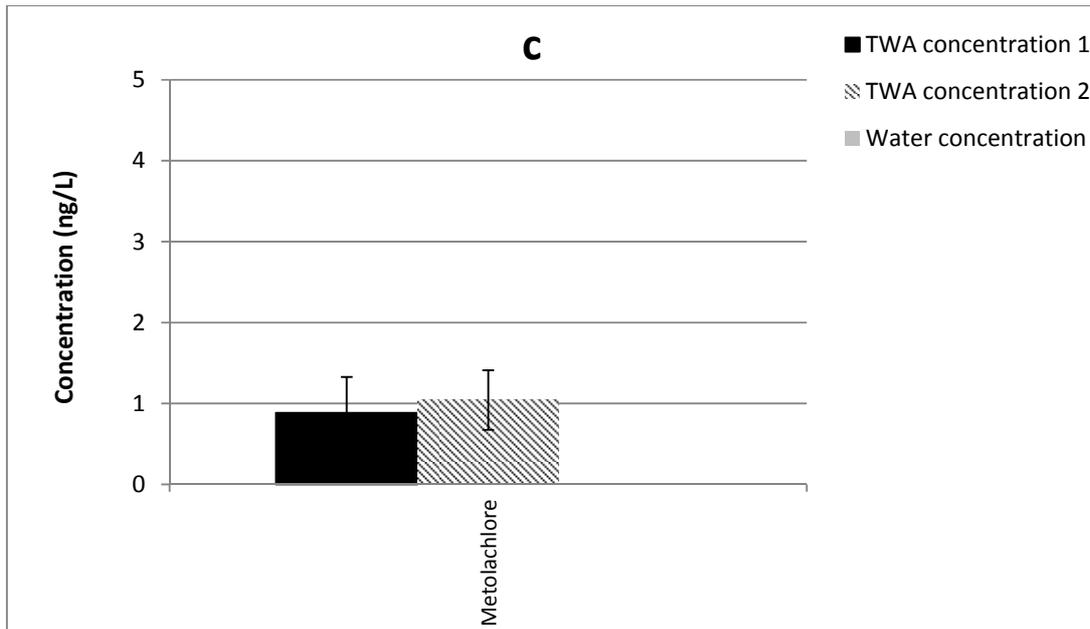


Figure 5: Comparison between TWA concentrations calculated with sampling rate from the literature (Table 2) and average concentrations in spot water samples in site 1. Errors bars represent standard deviation.





Figures 6A 6B 6C: Comparison between TWA concentrations in pesticides and pesticide concentrations in water in site 2 (n=2). Errors bars represent standard deviation.

Table 1: Sampling rates used for the estimation of TWA concentrations from Hernando et al., 2005; Alvarez, 2004 and Alvarez et al., 2007.

Sampling rates (Rs)	Rs (L/day) from quiescent renewals for POCIS (~228 mg, 41 cm²) in distilled water	Rs (L/day) from quiescent renewals for POCIS (~200 mg, 41 cm²) in sea water
Atrazine	0.05	0.053
DEA	-	0.022
Simazine	-	0.047
Diuron	0.011	0.023