Deltamethrin in sediment samples of the Okavango Delta, Botswana

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Abstract

Deltamethrin concentrations were determined in 35 sediment samples collected from three different habitats: channel, lagoon and pool sites from Xakanaxa in the Okavango Delta, NW Botswana. The samples were Soxhlet-extracted in acetone to extract deltamethrin residues and subsequently cleaned-up with silica gel 60. The final determination was carried out with a gas chromatograph equipped with an electron capture detector (GC-ECD). The sample work-up and determination gave deltamethrin recoveries of 54 to 97%, and detection limits of 0.004 mg/kg dw. The concentration of deltamethrin residues in the sediment samples collected from the three sprayed areas in the Okavango delta ranged between 0.013 and 0.291 mg/kg dw, with the highest concentrations observed in samples obtained from the pool sites. Analysis of samples for organic matter content showed percentage total organic carbon (% TOC) ranging between 0.19% and 8.21%, with samples collected from the pool having the highest total organic carbon. The concentrations of deltamethrin residues and the % TOC in sediment samples showed a similar trend with the highest levels recorded in the pool samples. These data confirmed that a simple method based on GC-ECD, after Soxhlet extraction, was robust enough to enable quantification of deltamethrin in the sediments, because comparable results were obtained with a more sophisticated system consisting of a GC coupled to a mass spectrometer with a time of flight (TOF) analyser.

Keywords: Okavango Delta, chromatography, sediments, deltamethrin

Introduction

The Okavango Delta, situated in north-western Botswana, is a large alluvial fan with a wetland located in a semi-arid environment (Fig. 1). The wetland has a rich biodiversity that has attracted national and international concern over its preservation. The near pristine aquatic ecosystem was listed in 1996 as a RAMSAR site, a wetland of international importance (Ramberg, 1997). The designated area (65 000 km^2) of the site makes it the largest designated RAMSAR site in the world (Ashton and Neal, 2003; RAMSAR, 1971). Nevertheless, some parts of the delta are experiencing rapid changes such as drying which may be linked to both natural (i.e. tectonics and channel blockages) and anthropogenic causes. The environmental impact of pesticide application to control tsetse fly populations in the Okavango Delta is not well quantified.

Pesticide use in the Okavango Delta has varied in the past. Dieldrex was used in 1964; this was followed by dichlorodiphenyltrichloroethane (DDT) during 1967 to 1970. From 1972 to 1991, endosulfan was initially used alone, and then a mixture of endosulfan and deltamethrin was used, starting in the 1980s (Kgori, 2001). Since 2001, deltamethrin [(S)-alpha-cyano-3-phenoxybenzyl (1R)-cis-3-(2, 2-dibromovinyl)-2, 2-dimethylcyclopropane-carboxylate], a synthetic pyrethroid insecticide (Pham et al., 1984) has been used in controlling tsetse fly populations. Deltamethrin is widely used in agriculture (such as in Mexico) due to its persistence, residual activity and low toxicity to mammals (Laskowski, 2002). However, deltamethrin has been found to be very toxic to terrestrial invertebrates, fish and other aquatic organisms (Amweg et al., 2005; Pawlisz et al., 1998).

Once a compound such as deltamethrin enters the environment, it will partition into various components of that environment, based on the physical and chemical properties of the compound and the prevalent environmental conditions (Pawlisz et al., 1998). Deltamethrin has a vapour pressure of 0.002 mPa, and a water solubility of less than 2 µg/ℓ. The log octanol-water partition coefficient (Log_{kow}) is 5.4 (Kidd and James, 1991), which results in deltamethrin being highly lipophilic. This has a significant impact on the partitioning of deltamethrin into biota. Given the Log_{kow} of deltamethrin, the compound would most likely partition into sediments (both suspended and bed-load), biota and vegetation. A few studies have been conducted on the environmental fate, persistence and degradation of deltamethrin (Yanez et al., 2002; Ernsfed, 1999; Maguire et al., 1989, Muir et al., 1985,) and these have confirmed that sediments act as a sink for deltamethrin, and some losses, especially in pond environments, were due to volatilisation. Additionally, it has a very short half life in water (ranging between 8 to 48 h) and degrades to decamethrinic acid, as well as to its less active isomers. Additionally, deltamethrin bioconcentrates in aquatic animals but does not biomagnify up the food web. A study conducted in the Okavango Delta in 2001 (Huntsman-Mapila et al., 2002) found that peat samples become enriched with deltamethrin, but that there is a high degree of variation in results from sediment samples collected within 1 m^2, suggesting that deltamethrin is not uniformly distributed, possibly due to heterogeneity in the sediments, leading to differing degradation rates. The variable rate of degradation would therefore affect its degree of accumulation.

The heterogeneity of the sediment also makes the detection and quantification of low concentrations of insecticide residues a difficult task. For example, due to interferences from other organic substances in the sample, extensive sample preparation

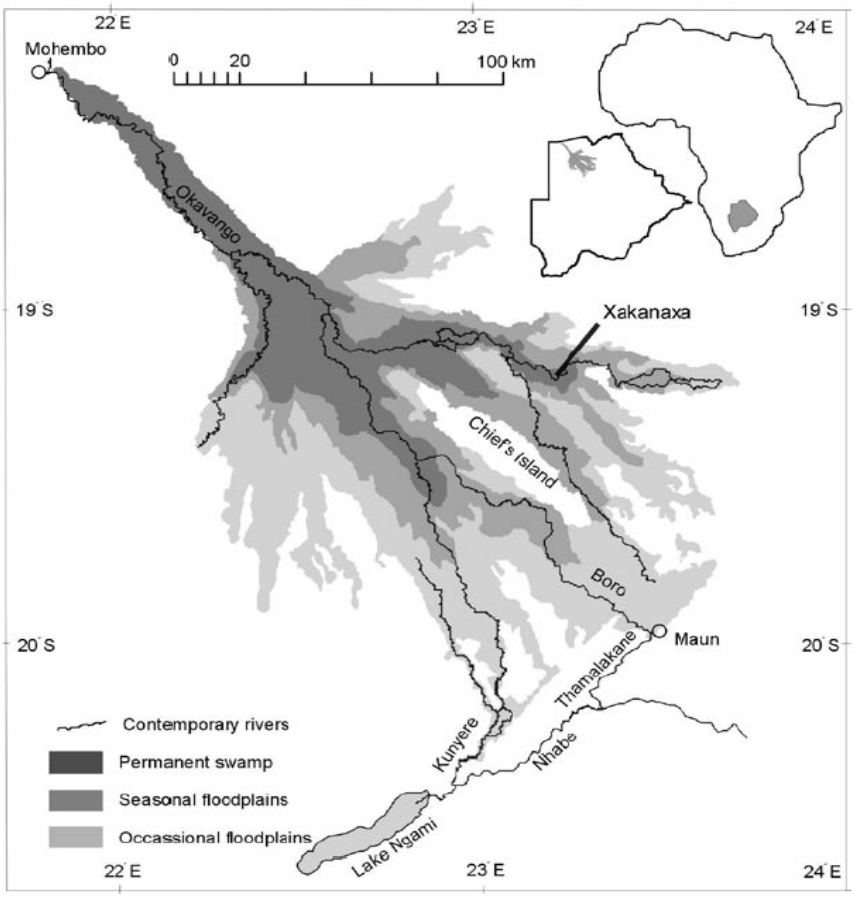

Figure 1
Alluvial fan of the Okavango Delta showing the location of Xakanaxa

has to be carried out prior to determination of the insecticide residues using gas chromatography or high performance liquid chromatography (Arrebola et al., 1999; Matovská and Lehotay, 2004; Ramesh and Ravi, 2004). Sample preparation may even involve hydrolysis followed by derivatisation (Schettgen et al., 2002), which may further complicate the analysis. The aim of this study was to use a simple sample work-up for the gas chromatographic determination of deltamethrin contamination of sediments in the Okavango Delta.

Methods

Reagents and materials

A certified deltamethrin standard (99.0% pure) was obtained from Dr Ehrenstorfer's laboratory (Augsburg, Germany). A stock solution of deltamethrin (1 000 mg/ℓ) was prepared in hexane. Calibration standards (0.010 to 0.250 mg/ℓ) were prepared by dilution. All stock and standard solutions were freshly prepared and stored at 4°C. Silica gel 60 was obtained from Fluka Chemicals and was dried at 120°C overnight prior to use.

Sample site and sampling

The sediment samples were collected from July to August of 2002. At the time of sample collection, the study area had been sprayed 4 times, with approximately 10 days between each spraying event. The spray concentrate used during this spray campaign consisted of 3.57 g/ℓ of the active ingredient in a carrier of 325 mℓ/ℓ of Fluid-AR 150 (a heavy aromatic petroleum-based solvent) and 673 mℓ/ℓ of sunflower oil. The application rate was 0.26 g/ha of active ingredient for each spray cycle (Huntsman-Mapila, 2002).

Sediment samples were collected on days 1 to 5 and day 17 following the overnight 5th spraying event. A sediment sample used for the determination of percentage total organic carbon (%TOC) was collected the day before the 5th spray event. All sediment samples were collected using a Van Veen grab (Stubbs et al., 1987). Samples were individually wrapped in aluminium foil, packed in airtight polythene bags and stored at -10°C until further handling and subsequent analysis. All the analyses were done in the Chemistry laboratory, University of Botswana, except for the GC/MS analysis which was carried out by Leco laboratories, South Africa.

Samples were collected from the following three different habitats near Xakanaxa, within the Moremi Game Reserve (see Fig. 1).

- Channel – a narrow sedge/reed/grass lined channel with clean Kalahari sands as bottom sediments (Sites S9 and S10)
- Lagoon – a shallow (< 1 m) sedge and lily filled lagoon with organic rich sediments overlying Kalahari sands (Sites S7 and S8)
- Pool – a deeper (< 2 m) pool with a thick layer of soft anoxic organic rich sediments (Sites (S1 and S2).

This site near Xakanaxa was selected as a detailed investigation of the impact of the spraying on aquatic organisms was also being conducted here, and the three habitats representative of the different sediment compositions were selected, i.e. the sandy sediments in the channel, the organic-rich sediments in the lagoon and the anoxic organic-rich sediments in the pool area, respectively. Measurements of pH, dissolved oxygen (DO), conductivity and temperature of the water at each habitat were measured *in situ* using the appropriate meter.

Analysis

Gas chromatography

Gas chromatographic analyses were carried out using a Perkin Elmer Auto system gas chromatograph (Norwalk Connecticut, USA), fitted with a fused silica capillary column (5% phenyl-polysiloxane) Zebron ZB 5: 30m long, 0.25 mm ID x 0.25 µm film thickness. All 1 µℓ samples were injected manually using a syringe in the split-less injection mode. The oven temperature programme was raised from 50°C to 300°C at a ramp of 45°C/min and held at 300°C for 11 min. The injector temperature was set at 250°C, and detector temperature set at 300°C.

Identification of deltamethrin in the sediment samples was carried out with a GC coupled to a mass spectrometer equipped with a time of flight (TOF) analyser. Cleaned up aliquots of the extracts were sent to Leco laboratories in South Africa. The GC column was employed with the following conditions; HP 5 column 20 m x 0.18 mm ID, 0.18 µm film, oven temperature 50°C to 325°C at 20°C/min, held for 5.25 min. Helium was the carrier

TABLE 1
Concentration of deltamethrin residues in selected sediment samples determined by GC ECD and GC TOF-MS

Sample	Sampling time subsequent to spray event	Concentration of deltamethrin (mg/kg dw)	
		GC-ECD	GC TOF-MS
Lagoon S7	Day 3	0. 048	0.02
Lagoon S7	Day 17	0.020	0.03
Channel S9	Day 3	0.017	0.02
Channel S10	Day 17	0.013	0.02
Pool S1	Day 17	0.221	0.20

For all analyses, n = 3 and RSD less than 11% for ECD and RSD less than 5% for TOF-MS.
dw = dry weight

gas at 1.0 mℓ/min constant flow and an injection volume of 1 µℓ. The ion source was maintained at 250°C, transfer line temperature was 260°C, and a LECO Pegasus III TOF mass analyser was used. Aliquots of a subset of 5 samples from the population of 35 was quantitatively analysed with both GC-ECD and GC TOF-MS in order to compare the two methods (see Table 1).

Determination of total organic carbon in sediments

The total organic carbon (%TOC) was determined using a modified Walkley-Black (Heanes, 1984) method. Dry sediment samples (0.50 g) were weighed into 500 mℓ conical flasks. 10 mℓ of a 2 N potassium dichromate solution was added to the weighed samples, followed by 20mℓ of concentrated sulphuric acid with continuous swirling to ensure mixing. The mixture was left in a fume hood for 1 h. An aliquot of 200 mℓ of a flocculant, Superflock 127 solution was added to samples to coagulate the soil particles, and the mixture was left standing in the fume hood overnight. Seven standard sucrose solutions (0.00, 0.004, 0.006, 0.008, 0.012, 0.016 and 0.024 g carbon), and a reference soil sample, were treated in the same way. Absorbance measurements of the standards and the samples were taken at 620 nm, employing a Shimadzu UV-Visible spectrophotometer. A calibration curve of absorbance vs. concentration of the sucrose standards was prepared and used to determine the % TOC in the samples.

Moisture content determination

Moisture content of the sediments was determined using a standard method. Sub-samples (ca. 5 g) were weighed in evaporation dishes and placed in a drying oven at 110°C, and dried to constant mass. The dried sub-samples were re-weighed and the water content in each sample determined.

Extraction and clean-up procedures

A modified Bligh and Dyer (1959) method was used for extraction of the samples. Acetone, dichloromethane and hexane were investigated for their suitability to extract deltamethrin from sediment samples using Soxhlet and sonication extraction techniques. A dried and weighed sub-sample (5 g) was mixed with an equivalent amount of anhydrous sodium sulphate and spiked with deltamethrin (5 mg/kg) and aldrin (0.020 mg/kg; internal standard). The samples were either Soxhlet-extracted for 4 h, or sonicated using an ultrasonic bath (Nurenberg, Germany) for 30 min, with each of the three solvents. Extractions were performed in triplicate.

The solvents were evaporated to near dryness using a rotary evaporator. The extracts were re-dissolved in 5 mℓ dichloromethane and aqueous sodium chloride (5% w/v) was added. The dichloromethane layer was decanted out and dried over a column of anhydrous sodium sulphate. The solvent was evaporated under a stream of nitrogen gas. The dry extract was re-dissolved in 2 mℓ hexane and loaded onto a hexane conditioned silica gel column (Silica gel 60). A diethyl-ether: hexane (4 mℓ; 2: 98, v/v) mixture was passed through the column as a clean-up solvent and the deltamethrin residue was eluted with diethyl-ether: hexane (10 mℓ; 3:7, v/v). The eluate was dried under a stream of nitrogen and then re-constituted in 1 mℓ hexane. The recoveries of the deltamethrin from sonication and Soxhlet extraction were evaluated by gas chromatography.

Evaluation of sample clean up materials for deltamethrin in sediment samples

Deltamethrin is a moderately-polar compound (Pawlisz et al., 1998); hence both polar and non-polar solid-phase extraction materials were investigated for their ability to isolate deltamethrin from the other components in the extract. Silica gel 60 packed in a short column was compared with C_{18} and florisil solid-phase extraction columns as described below:

Silica gel: A Pasteur pipette packed with 1 g silica gel 60, (0.04 to 0.063 mm particles) was conditioned with 6 mℓ hexane. A standard solution of deltamethrin (5 mg/kg deltamethrin) dissolved in 1mℓ hexane was loaded. Solvent mixtures of diethyl ether in hexane were investigated for their suitability to remove impurities. Mixtures of 20, 30 and 50% DEE in hexane were used to elute the deltamethrin from the silica gel column. The columns were washed with 2 to 6 mℓ portions of the solvents, and wash mixtures collected for deltamethrin analysis using GC. This step was followed by passing 2 to 6 mℓ solvent portions of the eluting mixtures, and the eluates collected, evaporated and re-dissolved in 1mℓ hexane, prior to injection into a GC system. A similar procedure was followed using Strata florisil cartridges (500 mg and 6 mℓ capacity), conditioned with 6 mℓ hexane.

Strata C_{18}: The Strata C_{18} column (500 mg/3mℓ capacity) was conditioned with 5 mℓ methanol and equilibrated with 5 mℓ deionised water. A standard solution of deltamethrin (5 mg/kg deltamethrin) dissolved in acetonitrile was loaded. Portions of the wash solvent mixture (2 to 5% methanol in deionised water) were passed through the column. The eluates were collected in different vials for GC analysis. Hexane and acetonitrile were also investigated for their suitability as eluting solvents for deltamethrin. 2 mℓ hexane was passed through the column and the eluates collected for analysis. The same procedure was repeated with acetonitrile as the eluting solvent. The eluates were subsequently dried under a stream of nitrogen and re-dissolved in 1 mℓ hexane, prior to injection into a GC system. In all extractions, recovery was evaluated in order to select the best SPE system.

Results and discussion

The results for sample preparation methods for recovery of deltamethrin from the sediments are presented, as well as concentrations of deltamethrin in the sediment samples collected from the Okavango Delta.

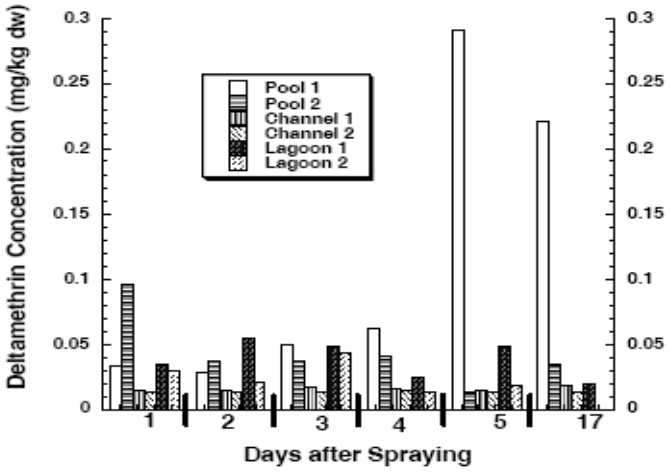

Figure 2
Concentration profile of deltamethrin over sampling days subsequent to the spray event from the channel, lagoon and pool sites. Analysis was carried using GC-ECD for n>6, with RSD < 6%. Sampling cycle was 10 d , and two samples were taken every day for 5 d from the same site, then on Day 17 after the spray cycle.

Optimisation of sample work up (extraction and purification)

Of the three solvent systems used for Soxhlet extraction of deltamethrin from spiked samples, acetone gave the highest recovery (mean recoveries of 54 to 97%, RSD less than 10%). Hexane and dichloromethane gave comparable, but lower recoveries of between 40 to 60%. High recoveries using acetone could probably be attributed to its high polarity, thereby improving its leaching capabilities.

Soxhlet and sonication extractions using acetone as the extracting solvent were compared. Soxhlet extraction gave better recoveries than sonication, which could be attributed to longer contact time (4 h) compared to the 30 min for sonication, and the refluxing which increases mass transfer of the analyte.
Silica gel, C_{18} and florisil materials were evaluated for their suitability to clean extracts. The following conditions were found optimum for the different sorbents: For florisil, 10 mℓ of diethyl ether: hexane (6:94, v/v) was found best suited for removing the impurities. Deltamethrin and aldrin (internal standard; IS) were eluted with 10 mℓ diethyl ether: hexane (3:7, v/v). For C_{18} SPE column, the best wash solvent mixture was 5% methanol in water and acetone as the eluting solvent.

Silica gel 60: The best wash solvent mixture was 4 mℓ of diethyl ether: hexane (2:98 v/v). The analytes were best eluted with 4 mℓ of diethyl ether: hexane (3:7, v/v). However, high recovery of 94% (RSD 7%) deltamethrin was achieved when silica was employed, compared to 21% (RSD 9%) and 14% (RSD 7%) recoveries obtained for C_{18} and florisil respectively.

Concentration of deltamethrin residues in the Okavango Delta after aerial spraying

A sub-set of sediment samples collected from Xakanaxa were analysed using both GC-ECD and GC TOF-MS using an aldrin internal standard. Table 1 shows a comparison of the concentration of deltamethrin in the selected sites for both techniques.

TABLE 2
pH, temperature and DO measured over the 5 days after the spray event

Location	Pool	pH	Temp (°C)	Oxygen (mg/ℓ)
Day	1	6.44	17.4	5.82
	2	6.48	19.2	4.53
	3	6.32	19.9	6.19
	4	6.54	18.9	5.40
	5	6.63	19.0	6.10
Location	**Lagoon**	**pH**	**Temp (°C)**	**Oxygen (mg/ℓ)**
Sampling time (days)	1	6.52	16.3	5.15
	2	6.48	18.8	3.31
	3	6.62	19.1	3.32
	4	6.37	16.8	3.90
	5	6.46	17.0	3.70
Location	**Channel**	**pH**	**Temp (°C)**	**Oxygen (mg/ℓ)**
Sampling time (days)	1	6.03	15.9	5.12
	2	6.5	17.6	3.73
	3		17.4	3.35
	4	6.48	17.0	4.3
	5	6.43	17.2	4.0

A two-tailed, t-test at 95% confidence level showed that there was no significant difference in the concentrations of deltamethrin residues for each sample as determined by the two techniques. However, GC-ECD was more sensitive, with detection limits (LOD) calculated to be 0.004 mg/kg, compared to 0.010 mg/kg for GC/TOF-MS. Therefore GC-ECD was chosen for the quantification of deltamethrin residues in samples.

Figure 2 shows the concentrations of deltamethrin in 35 sediment samples collected from Xakanaxa, analysed using GC-ECD. More than one sample was collected at each habitat (i.e. pool, lagoon and channel), and there was a high degree of variability, which revealed that the deltamethrin was not evenly distributed in the sediments. The figure also shows that the highest concentrations observed were from the pool sites, followed by the lagoon, with the channels exhibiting the lowest deltamethrin concentrations. The observed trend was expected due to the nature of the sediment samples, as the lagoon and pool sediments were found to be organic-rich clays, while the channel sediments were mainly sandy, hence poor retention of the deltamethrin. A similar adsorption phenomenon was demonstrated by Zhu and Selim (2002) in their laboratory simulation studies, which showed that deltamethrin had higher levels in clay soils, when compared with sandy soils, due to increased cation exchange capacity and decreased pH.

The concentration of deltamethrin residues in sediments is influenced by temperature, pH, dissolved oxygen (DO) and %TOC. Temperature has a direct impact on the degradation of deltamethrin and the amount of DO, which in turn affects the activity of micro-organisms (Laskowski, 2002; Schurer, 1985). The microbial degradation of an organic compound such as deltamethrin may contribute to the development of anoxic conditions in the water system, which is potentially detrimental to the ecosystem. The quantity of TOC in the sediments/soils depends on the amount of organic matter added, sediment texture such as clay content, and climatic conditions (Jenkinson, 1990). In order to account for the variation of deltamethrin residue concentrations between samples from different sites, physicochemical parameters such as temperature, DO and pH of water in the channel, lagoon and pool were recorded daily (see Table 2).

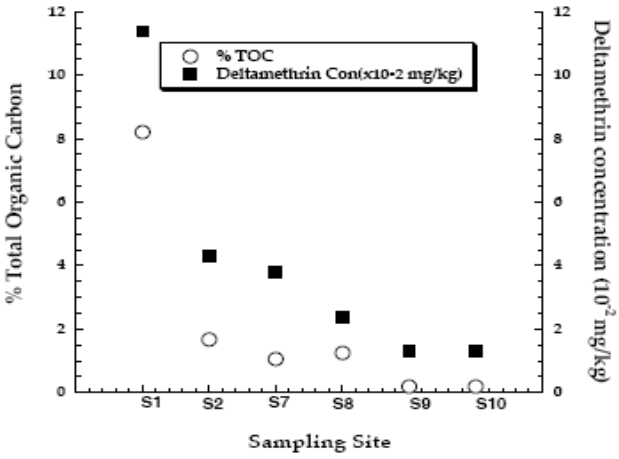

Figure 3

Correlation of % TOC with deltamethrin concentration in sediment samples collected from the Okavango after aerial spraying. S1 and S2 are pool samples, S7 and S8 are lagoon samples, S9 and S10 are channel samples. The RSD was less than 6% for all samples for n = 6.

TOC was also evaluated in the sediment samples to evaluate its influence on the concentration of deltamethrin in sediment samples (see Fig. 3).

The pH (near neutral for all the samples) and temperature showed that there was minimal variation in these two parameters between sites over the 5 d of sampling. It can therefore be concluded that these two parameters had insignificant influence on the concentration variations of deltamethrin residue between samples. However, DO values for the channel and lagoon were lower than those of the pool as monitored from day one to day five, which is unusual given the high level of organic rich sediments in the pool.

The TOC content of the sediments collected from the pool sites was highest, and this was reflected in the measured amounts of deltamethrin in the sediments (Fig. 3). Deltamethrin persisted in the environment, in particular in the pool habitat, as shown by the results from samples collected at intervals after the spraying event. The trends in the %TOC parallel those of deltamethrin residues concentrations in the sediments. Sediments collected from the pool showed an enhanced %TOC in the pool samples. The high carbon content may contribute to the high adsorption of deltamethrin, hence its persistence. The microbial action on an organic compound such as deltamethrin may contribute to the development of anoxic conditions in the water system, which is potentially detrimental to the ecosystem.

Conclusion

A method for the determination of deltamethrin residues in sediment samples collected from the Okavango Delta was developed with emphasis on sample preparation. Soxhlet extraction, employing acetone as the extracting solvent, was used for extracting deltamethrin from sediment samples, using silica gel 60 and hexane as well as diethyl ether for cleaning the sample extracts. The final determination of deltamethrin residues was carried out using GC equipped with electron capture detector (ECD), which was selective for the deltamethrin and with LOD, 0.004 mg/kg. The identity and concentration of deltamethrin were confirmed using GC-MS with a TOF mass analyser. The concentration of deltamethrin residues in the sediment samples collected from the sprayed areas in the Okavango delta ranged between 0.013 and 0.291 mg/kg, with the highest concentrations observed in samples obtained from the pool sites. Analysis for organic matter content of the samples showed that the concentration of deltamethrin increased with an increase in total organic carbon in sediment samples. It can therefore be concluded that variations in concentration of deltamethrin residues observed between samples was influenced by adsorption of deltamethrin on the organic carbon in the samples or that deltamethrin concentrations in the sediments enhanced to a small extent, the carbon content of the sediments. Temperature and pH had little influence on the variation of deltamethrin residue in different samples, as these parameters remained fairly constant between sites and days of sampling. The analyses of DDT and endosulfan an in the delta environment will form part of a separate study.

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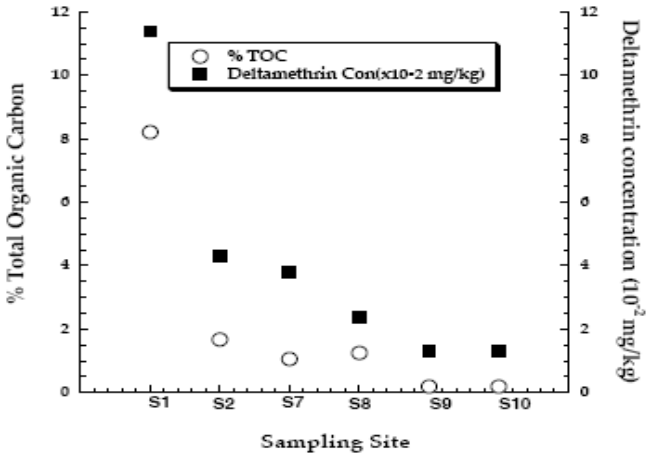

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