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Normal-phase high-performance liquid chromatography with UV irradiation, morin complexation and fluorescence detection for the determination of organotin pesticides

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ABSTRACT

A method has been developed for the determination of the organotin pesticides fentin, cyhexatin and fenbutatin oxide by high-performance liquid chromatography combined with UV photoconversion and post-column morin complexation followed by fluorescence detecton. After optimization of the relevant parameters the feasibility of the method for analysing environmental samples was investigated. Detection limits are 1–2 ng in standard solutions, 0.02–0.03 μg/l in surface water and 0.2–0.3 μg/g in soil and sediment. The higher detection limits for soil and sediment samples are due to interfering compounds present in the matrix. The method allows trace level determinations in water samples. As an example, in a ditch adjacent to a potato field 16 days after a routine spraying with triphenyltin acetate, water concentrations of 0.03 μg/l could still be detected.

INTRODUCTION

Organotin compounds are used as poly(vinyl chloride) (PVC) stabilizers and as biocides in agriculture and antifouling paints. The annual world-wide production of organotins amounted to 40 000 tons in 1986 [1]. Since the disastrous effects of the use of organotins [mainly tributyltin salts (TBT)] in antifouling paints on the oyster culture in the bay of Arcachon (France), where oyster production fell by 70% in 2 years [2] and similar problems on the southern English coast [3], the environmental risk of organotin-based antifoulings became recognized. In many countries such as France, the UK, the Netherlands and the USA, the use of organotin-based antifoulings is now restricted.

Another even larger deliberate input of organotin compounds into the environment occurs via their use as pesticides (Fig. 1) in agriculture. For example, in the Netherlands the annual use of fentin [triphenyltin acetate (TPT)] on potato crops was 300 tons of active compound in 1987[4]. This represents 8% of the total amount of fungicides used in agriculture in the Netherlands [5]; actually, compared with organotin-based antifoulings, three times more organotins were used in agriculture than in antifoulings in 1985 [1]. Fenbutatin oxide [hexakis-(2-methyl-2-phenylpropyl)distannoxane, FBTO] and cyclohexyltin compounds [cyhexatin; tricyclohexyltin hydroxide or azocyclotin; tricyclohexyltin-1,2,4-triazole (TCT)] were used in much more limited amounts, *viz.* 8 and 1 tons, respectively, in 1987.

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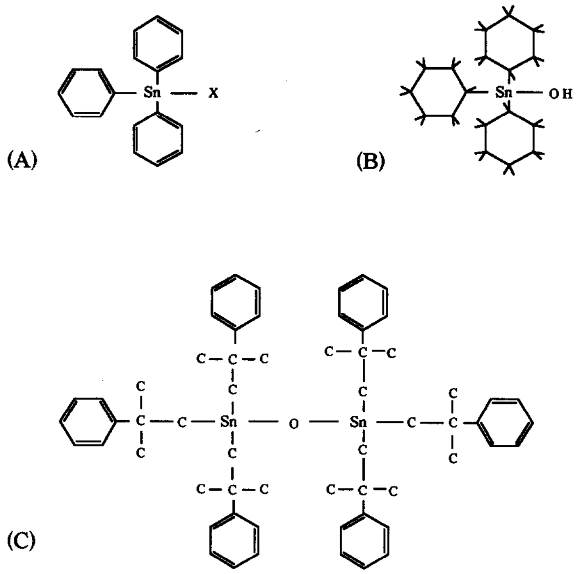

Fig. 1. Structural formulae of organotin pesticides. (A) Triphenyltin (TPT), for fentin, X = acetate. In the environment X is rapidly exchanged for a hydroxide ion. In the current study triphenyltin chloride (X = Cl) was used. (B) Tricyclohexyltin hydroxide, cyhexatin (TCT). (C) Fenbutatin oxide (FBTO). In the environment the dimeric form decomposes rapidly to the monomeric (hydroxide) form.

FBTO is mainly used on tomatoes and cucumbers and TCT is used on apples [4].

Sensitive techniques for the determination of organotin residues are essential in view of the environmental hazards. Several techniques exist for the determination of butyltin compounds. Gas chromatographic (GC) methods commonly rely on alkylation or hydride formation to obtain volatile derivatives. Several detection techniques can be applied: flame photometric [6,7], atomic absorption spectrometric (AAS)[8,9], mass spectrometric (MS) [10,11] and atomic emission detection [12].

High-performance liquid chromatography (HPLC) can handle more polar compounds than GC, therefore no derivatization prior to chromatography is needed. Unfortunately, common HPLC detectors do not offer the required sensitivity and selectivity. Some workers have used HPLC combined with specific detection techniques, such as graphite furnace AAS [13–16], hydride formation and quartz furnace AAS [17] or hydride formation–d.c. atomic emission spectrometry [18]. A drawback of these techniques is that they require complicated interfacing of the HPLC effluent to the detector.

Another approach is to use post-column reaction detection where the organotin compounds are converted into products that are more easily detected by conventional HPLC detectors. Work has been done on oxine (8-hydroxyquinoline) and morin (3,5,7,2′,4′-pentahydroxyflavone) complexation of organotin compounds. Oxine yields complexes that are usually determined with UV absorption detection [19,20]. Morin forms complexes that show strong fluorescence [21–25]. Langseth [21] used pre-/on-column complexation and Yu and Arakawa [22] used post-column morin complexation followed by fluorescence detection, but both only applied this technique to di- and monoorganotins. For triorganotin pesticides the formation of such complexes is not favourable, because the tin atom is shielded by bulky carbon chains. In this work, HPLC of triorganotins was combined with UV irradiation to cleave some of the carbon-tin bonds to obtain a product that can be complexed with morin.

A similar approach was used by Lakata *et al.* [19], who used oxine complexation and UV detection, reporting detection limits of 0.1–0.5 μg for several di- and triorganotins, except dibutyltin (DBT), which yielded a detection limit of 40 ng. As reported detection limits for morin complexes of diorganotins are much lower, with values in the range of 2 pg–1 ng [22,25], morin seems to be a better alternative than oxine, and was therefore used in the present study.

EXPERIMENTAL

Materials

Di-*n*-butyltin dichloride (DBT), diphenyltin dichloride (DPT) (96% purity), triphenyltin chloride (TPT) (95% purity) and morin (3,5,7,2′,4′-pentahydroxyflavone) were obtained from Aldrich (Steinheim, Germany). Tri-*n*-butyltin acetate (TBT) was a gift from the Community Bureau for Reference (BCR) (Brussels, Belgium). Dicyclohexyltin dibromide (DCT) was purchased from Johnson Matthey Alfa (Karlsruhe, Germany). Cyhexatin (tricyclohexyltin hydroxide, TCT) (99% purity) was from Dr. Ehrenstorfer (Augsburg, Germany) and fenbutatin oxide (FBTO) (99.7% purity) was a gift from Atochem (Vlissingen, Netherlands). Ethanol

(HPLC grade), *n*-hexane (HPLC grade), tetrahydrofuran (THF) (HPLC grade), toluene (analytical-reagent grade), glacial acetic acid (analytical-reagent grade) and anhydrous sodium sulphate (Baker grade) were purchased from Baker (Deventer, Netherlands). Disposable cellulose nitrate filters (0.45 μm) for water filtration were supplied by Nalge (Rochester, NY, USA); 0.2-μm membrane filters (Rotrand) from Schleicher & Schüll (Dassel, Germany) were used to filter extracts before injection into the HPLC system.

Apparatus

The HPLC equipment consisted of a Kontron (Zürich, Switzerland) Model 410 single-piston pump or a Pharmacia (Uppsala, Sweden) LKB 2150 dual-piston pump, set at a flow-rate of 1 ml/min and equipped with a membrane pulse damper, a laboratory-made six-port injection valve with a 28-μl injection loop and a 15 cm × 4.6 mm I.D. stainless-steel column packed with 3- μm cyanopropyl-bonded silica (Rosil Alltech, Zwijndrecht, Netherlands). The laboratory-made UV irradiation reactor contained a medium-pressure mercury lamp and was described by Scholten *et al.* [26]. The irradiation coil (length 76, 125 or 255 cm) and reaction coil (length 27 or 85 cm) were made of 0.5 mm I.D. × 1.5 mm O.D. PFTE. A Valco (Houston, TX, USA) low-dead-volume T-piece was used as a mixing device. The reagent pump was a Labotron LDP-13 (Kontron) glass syringe pump delivering 0.15 ml/min of morin in ethanol (concentration 2.5–600 μg/ml). A Perkin-Elmer (Beaconsfield, UK) LS-4 fluorescence detector was used for detection. The excitation wavelength was 430 nm and the emission wavelength 495 nm. Excitation and emission slits were set at a bandwidth of 15 and 20 nm, respectively. The set-up is shown in Fig. 2.

Extraction of water, sediment and soil

In order to study the selectivity of the method for organotin compounds in environmental matrices, field samples from different locations were taken for analysis. Straightforward extraction techniques were used. Sediment samples were taken from the Hertentocht canal in the Noordoostpolder at a location adjacent to apple orchards where TCT may be found and from an unpolluted location, Lake Maarsseveen, in the province of Utrecht. Soil samples were taken from the above mentioned apple orchard and from a potato field (Wiertocht), a location where TPT may be found, in the Oostelijk-Flevoland polder. The samples were taken in December 1990, at least 3 months after the spraying season. Surface water samples were taken in September 1991 just a few h and 16 days after field application of TPT from a ditch adjacent to a potato field near the village of Bant in the Noordoostpolder.

Surface water samples of 0.75 l were filtered through a 0.45-μm cellulose nitrate filter and spiked with 0.9 ml of toluene solution containing three organotin pesticides, TCT, FBTO and TPT, and were extracted twice with 40 ml of *n*-hexane by shaking for 5 min. The extracts were dried over anhydrous sodium sulphate and concentrated to *ca.* 2 ml in a Kuderna Danish concentrator prior to injection on to the HPLC column. Extracts were further reduced in volume to *ca.* 0.3 ml for trace-level determinations.

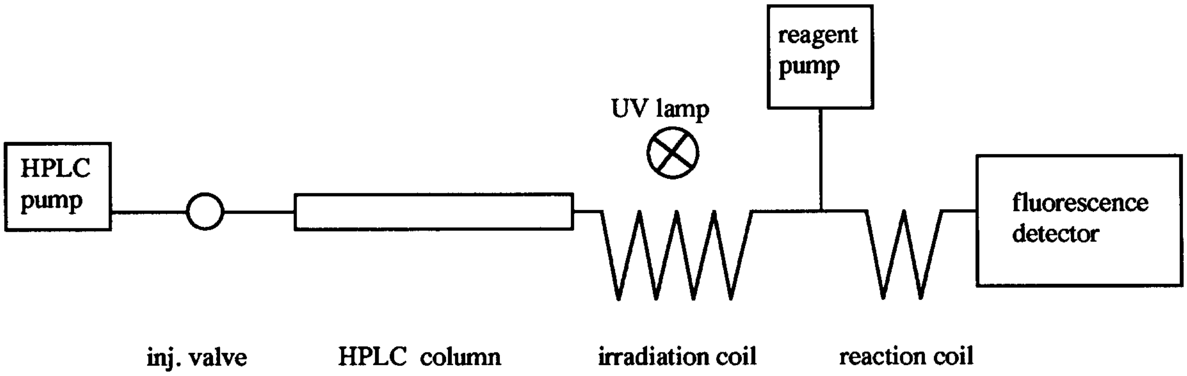

Fig. 2. Scheme of HPLC–reaction detection set-up.

Sediment and soil samples were wet-sieved through a 2-mm stainless-steel sieve and oven-dried at 105°C for 12 h. Amounts of 10 g of dry sediment or soil were spiked with 100 μl of toluene solution containing the organotin pesticides; adsorption was allowed to proceed for at least 4 h before extraction. Soxhlet extraction was carried out for 12 h using hexane–acetone (9:1) as extractant. The organic extracts were concentrated to *ca.* 4 ml in a Kuderna Danish concentrator, dried over anhydrous sodium sulphate and filtered through a membrane filter (0.2 μm) before injection. The injection volume was 28 μl in all experiments.

Non-spiked samples were used to study backgrounds and calculate attainable detection limits; spiked samples were used to calculate extraction efficiencies.

RESULTS AND DISCUSSION

Separation of the organotin compounds

Because of the high polarity of organotin halides, little or no retention can be achieved in reversed-phase HPLC [27]. Cyanopropyl-bonded silica columns have been used in several studies for the separation of organotin compounds in the normal-phase mode [21,22,27]. Because organotin compounds show strong interaction with residual silanol groups, different methods to mask this undesired phenomenon have been used. Periodic treatment of the column with iodine chloride as proposed by Praet *et al.* [27] proved to be unsatisfactory in our hands, giving irreproducible retention times and poor peak shapes. The addition of 0.5–5% of glacial acetic acid to the mobile phase gave good results. A mobile phase of *n*-hexane–THF–acetic acid (90:5:5) could be used for the separation of dialkyltin compounds but trialkyltin compounds showed only very little retention and eluted as one peak. The use of *n*-hexane–THF–acetic acid (96:2:2) gave good separation of the triorganotins except for TBT and TCT, which co-eluted. DBT and DPT can be separated in the same system. The use of a mobile phase of weaker elution strength, *n*-hexane–THF–acetic acid (98:1:1) or *n*-hexane–acetic acid (99.5:0.5), did not improve the separation of TBT and TCT.

Further work was done with *n*-hexane–THF–acetic acid (96:2:2) as mobile phase. Capacity factors of seven investigated organotin compounds are given in Table I, and a chromatogram of a standard mixture containing five organotins is shown in Fig. 3. DPT and, to a lesser extent, TPT have broader peaks than would be expected on the basis of their retention times. Carrying out the separation at 45°C instead of at ambient temperature did not improve the peak shapes.

TABLE I

CAPACITY FACTORS (k') AND DETECTION LIMITS OF SEVEN ORGANOTIN COMPOUNDS USING STANDARD SOLUTIONS

Organotin compound	k'	Detection limit (ng)
TCT	0.2	2
TBT	0.2	30
FBTO	0.6	1
TPT	1.5	1.5
DCT	1.4	0.5
DBT	2.8	0.6
DPT	5.6	0.6

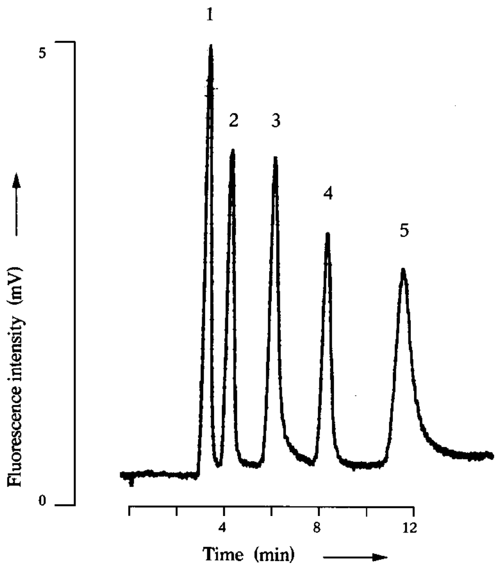

Fig. 3. HPLC of a standard mixture of organotin compounds. Column, 15 cm × 4.6 mm I.D. Rosil 3-μm cyanopropyl; mobile phase, *n*-hexane–THF–acetic acid (96:2:2); flow-rate, 1.0 ml/min; irradiation coil, 76 cm; reaction coil, 27 cm; reagent flow-rate, 0.15 ml/min of morin solution in ethanol (25 μg/ml). Peaks: 1 = TCT (0.8 μg); 2 = FBTO (0.7 μg); 3 = TPT (0.8 μg); 4 = DBT (0.8 μg); 5 = DPT (0.9 μg).

Optimization of the reaction detection system

Optimization of the reaction detection system was carried out for DBT, TBT, DPT and TPT. The HPLC eluent flow-rate was kept constant at 1 ml/min and the reagent pump flow-rate at 0.15 ml/min. Initial experiments were done by flow-injection analysis (FIA), to find near-optimum conditions. A 0.5 mm I.D. × 1.5 mm O.D. PFTE capillary was used as the irradiation coil. PFTE with a thinner wall thickness (0.3 mm I.D. × 0.8 mm O.D.), which has better UV transparency, was not satisfactory because it became brittle after a few h.

In the literature there is no consensus on the question of whether diorganotins [28] or monoorganotins [21] yield the highest fluorescence response with morin. Triorganotins and tin(IV) are reported to show relatively weak fluorescence. An optimum irradiation time is therefore expected to occur when the triorganotins are only partly degraded by UV light. The results presented in Fig. 4. show that TPT, TBT and DBT give the highest response when using the shorter 76 cm irradiation coil. With DPT there is some gain when using a coil length of 125 cm. The behaviour of DPT and DBT is not well understood. The response optimum for DPT at 125 cm seems to indicate that MPT forms a stronger fluorescent complex than the diorganotin, but the same effect is not found with DBT. The triorganotins behave as is expected: at a certain irradiation time, presumably corresponding to the photodegradation to a di- or monoorganotin, a response maximum is reached. When the compounds are exposed to UV light for a longer period of time, products are formed (mono-organotins or inorganic tin) that form less strong fluorescent complexes with morin. The 76-cm irradiation coil, which yields an irradiation time of 9 s, was used in subsequent studies.

For batch experiments optimum morin concentrations of 10–30 μg/ml in *n*-hexane–ethanol (85:15) were reported by Arakawa *et al.* [28]. Using the set-up shown in Fig. 2, we used morin concentrations of 2.5–600 μg/ml in ethanol as the reagent solution, which corresponded to morin concentrations of 0.32–78 μg/ml in the eluent. Fig. 5 shows that the lowest concentration of morin gives the highest response for TPT and DPT. For the determination of butyltin compounds higher concentrations appear to be more favourable. With standard solutions, however, no compounds competing for morin are present, as will certainly be the case with real envi-

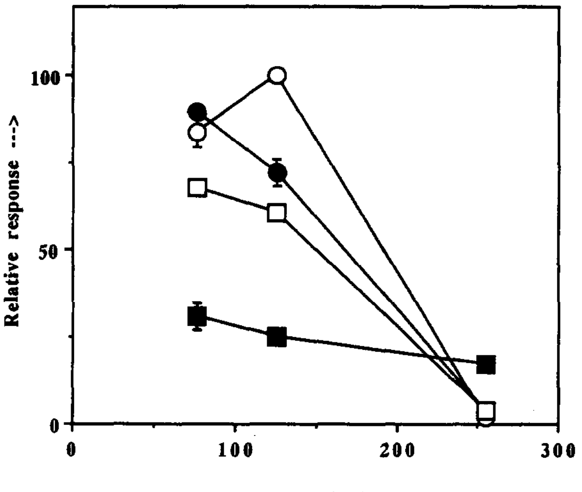

Fig. 4. Effect of irradiation coil length on fluorescence response of four organotin compounds in FIA. Organotin compounds: ● = TPT (1.7 μg); ○ = DPT (1.4 μg); ■ = TBT (3.0 μg); □ = DBT (1.3 μg). Mobile phase, *n*-hexane–THF (95:5); morin concentration after dilution with mobile phase, 0.33 μg/ml; reaction coil, 85 cm.

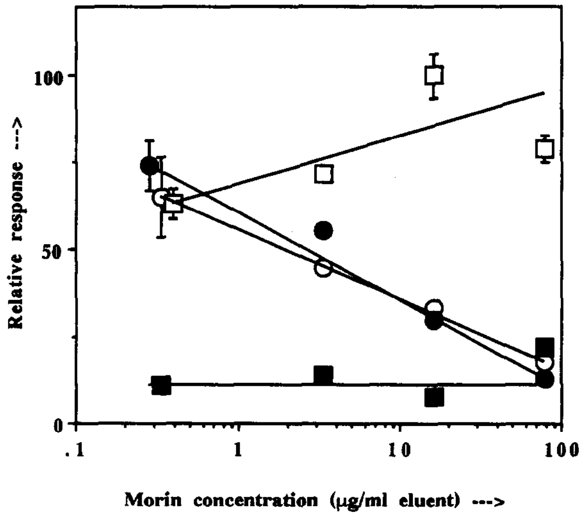

Fig. 5. Effect of morin concentration (after dilution with mobile phase) on fluorescence response of four organotin compounds. Column, 15 cm × 4.6 mm I.D. Rosil 3-μm cyanopropyl; mobile phase, *n*-hexane–THF–acetic acid (96:2:2); irradiation coil, 76 cm; reaction coil, 85 cm. Organotin compounds: ● = TPT (1.7 μg); ○ = DPT (1.4 μg); ■ = TBT (3.0 μg); □ = DBT (1.3 μg).

ronmental samples. We therefore used a morin concentration of 25 μg/ml, corresponding to 3 μg/ml in the mobile phase, for further investigations. In these experiments, the reaction coil length was 85 cm. Further work revealed that this length could be reduced to 27 cm (reaction time 2.8 s) without any decrease in response. The 27-cm reaction coil was used in further work.

Band broadening due to reaction detection was determined by comparing the variance (σ^2) observed for the preformed morin–DBT complex using the final set-up with the variance observed when injecting the complex on to the HPLC column directly connected with the fluorescence detector. High concentrations had to be injected because the complex turned out to be unstable on the cyanobonded column. The contribution of reaction detection to variance was calculated by means of the equation

$$\sigma^2_{\text{total}} = \sigma^2_{\text{reaction detection}} + \sigma^2_{\text{direct detection}}\ (s^2) \qquad (1)$$

Variances of the peaks were calculated using the method of Foley and Dorsey [29].

Band broadening due to reaction detection was found to be 7.1 ± 0.7 s. This is in line with the value of 5.5 s calculated for the irradiation plus reaction coil, neglecting the contribution of the T-piece, according to the equation [30]

$$\sigma_t = [(t_r d_t^2)/(96 D_m)]^{0.5} \qquad (2)$$

where D_m is the molecular diffusion coefficient of the analyte in the eluent (for this calculation a value of 10^{-9} m^2/s was taken), t_r is the residence time in the irradiation plus reaction coil and d_t is the inner diameter of the coils. The contribution of the reaction detection system to band broadening is higher than the experimental value of 4.2 s reported by Lakata *et al.* [19]. For the present system dimensions, *ca.* 40% of the final peak width of TPT is caused by the reaction detection part. Although this result can be improved to a certain extent by using knitted coils, no attempt was made to do so, as even complete elimination of band broadening due to reaction detection will effect less than a two-fold increase in sensitivity.

Analytical data

Detection limits for seven organotin compounds were determined at a signal-to-noise ratio of 3:1 and are given in Table I. The calibration plots were linear (within 10%) over two decades from the detection limit. The data are in line with the results found by Yu and Arakawa [22], who reported detection limits of 0.1–1 ng for dialkyltins in a similar system with postcolumn morin addition. In contrast, Langseth [25] reported much lower detection limits (2–6 pg) for dialkyltins in a system in which morin was added dissolved in the mobile phase. The difference between our work and that of Yu and Arakawa on the one hand and that of Langseth on the other cannot be explained completely. Factors influencing the results may be differences in the complex formation conditions, *i.e.* post-column *vs.* pre-/on-column, mobile phase composition and the quality of the detector used.

The repeatability of the method was found to be within 15% for all compounds and matrices investigated. Some drift in detector response was observed, which was due to contamination of the detector cell, flushing the detector with acetone and *n*-hexane restored the original response.

Determination of organotins in surface water

In monitoring programmes, water samples are usually filtered before analysis to eliminate differences due to varying loads of suspended matter. For a quick screening procedure, however, a method should preferably determine the total load of contaminant in the water. The present method was therefore tested with both filtered and non-filtered water samples. Recoveries at two spiking levels and detection limits were determined in triplicate and are given in Table II. Non-filtered water gives slightly lower recoveries than filter water at the same spiking level. It is known that triorganotins show strong sorption to particulate matter. Apparently the sorbed organotins are only partly extracted by *n*-hexane.

Experiments with surface water samples from different locations showed that the *n*-hexane extracts could be concentrated until the amount injected corresponded to *ca.* 60 ml of surface water, before background peaks became visible. Fig. 6A shows the chromatogram of a filtered water sample that was taken from a ditch (location Bant) a few h after the adjacent field had been sprayed with TPT. TPT was found at a level of 7 ± 3 μg/l in non-filtered water and at 2.9 ± 0.3 μg/l in filtered water. Water

TABLE II

RECOVERIES AND DETECTION LIMITS OF THREE ORGANOTIN COMPOUNDS IN SPIKED SURFACE WATER

Results are means ± standard deviation for triplicate determinations.

Analyte	Non-filtered water		Filtered water				Detection limit (μg/l)
	Spike (μg/l)	Recovery (%)	Spike (μg/l)	Recovery (%)	Spike (μg/l)	Recovery (%)	
TCT	13	86 ± 10	13	114 ± 20	2.9	67 ± 3	0.03
FBTO	6.7	70 ± 10	6.7	97 ± 15	1.5	61 ± 3	0.02
TPT	8.2	72 ± 23	8.2	101 ± 32	1.0	80 ± 10	0.02

samples were taken again 16 days after spraying; in the meantime no organotins had been applied. TPT could still be detected at a level of 0.02–0.04 μg/l in filtered water (see Fig. 6B). In our laboratory another method based on pentylation followed by GC–MS is being developed. For confirmation the same sample was analysed by this technique and the concentration of TPT was found to be 0.015–0.02 μg/l. The main advantage of the HPLC method is that it is much faster and requires less sophisticated equipment.

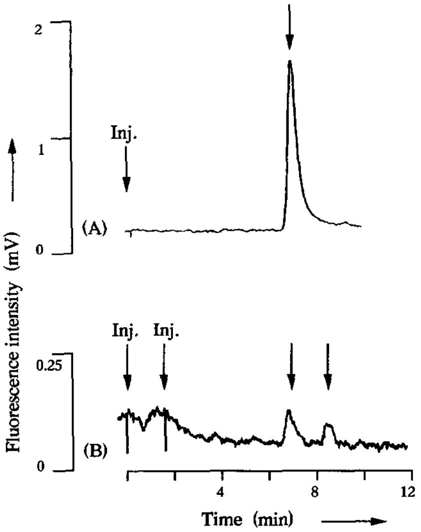

Fig. 6. (A) HPLC of filtered surface water (Bant) (amount injected corresponds to 8.0 ml of surface water) sampled a few h after the adjacent potato field had been sprayed with TPT (concentration found: 2.9 ± 0.3 μg/l). (B) HPLC of two injections of a sample taken at the same location 16 days later (amount injected corresponds to 66 ml of surface water) TPT (see arrows): 0.02–0.04 μg/l. Conditions as in Fig. 2.

Determination of organotins in sediments and soils

Preliminary studies were carried out to assess the potential of the present method for the determination of organotins in sediment and soil samples. Fig. 7 shows some typical examples. Fig. 7A shows a chromatogram of a Wiertocht soil. If the peak observed at the retention time of TPT (6.5 min) is indeed due to this compound, it represents a concentration level of about 0.4 μg/g (however, also see below). Similar chromatograms were obtained for a Hertentocht soil sample (data not shown). Fig. 7B shows the chromatogram of a Hertentocht sediment. Obviously, in this instance the background is too high to allow any meaningful conclusion, especially because the organotins of interest elute in the same retention time range as do the major background peaks. Actually, the Hertentocht sediment with its high organic matter content can be considered as a worst-case example. The Maarsseveen sediment, which has a lower organic content, gave chromatograms that were similar to those of the soil samples. Further study revealed that the background peaks originate from fluorescent compounds present in the matrix and not from compounds that form fluorescent complexes with morin. This was verified by filling the reagent pump with pure ethanol instead of the morin solution. An injected sediment sample gave identical background peaks as with added morin.

Despite the unfavourable situation, recovery data (peak heights of spiked vs. non-spiked samples) and detection limits (signal-to-noise ratio 3:1) were collected to obtain an approximate idea of the potential of the method (Table III). Obviously, the recovery is satisfactory in all instances. Detection limits typically vary between about 0.2 and 3 μg/g.

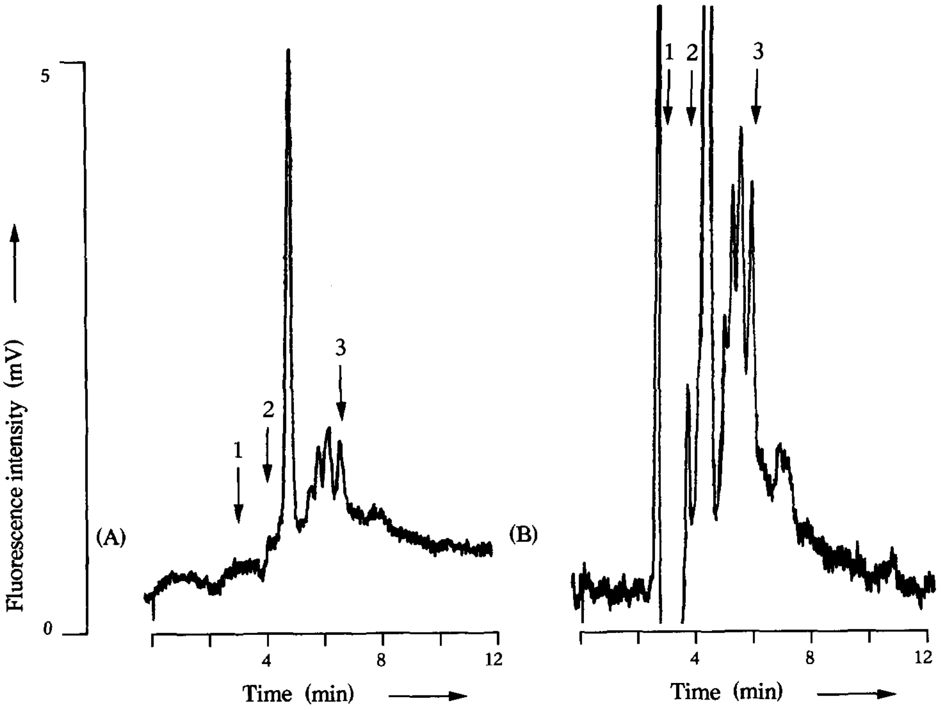

Fig. 7. (A) HPLC of a soil extract (Wiertocht) (amount injected corresponds to 55 mg soil). Retention times of the organotins are indicated: 1 = TCT; 2 = FBTO; 3 = TPT. (B) HPLC of sediment extract (Hertentocht) (amount injected corresponds to 60 mg of sediment). Conditions as in Fig. 2.

Reported sediment concentrations of TPT in a marina, originating from antifouling paints typically vary from 0.01 to 0.2 μg/g [31]. Values of 0.2–4 μg/g have been found in sediment adjacent to a potato field [32]. TCT concentrations after application in apple orchards were in the range 0.02–0.4 μg/g in sediments [33] and 0.07 μg/g in soils [34]. On the basis of these few reported field study data, the detection limits for soils and sediments obtained with the proposed HPLC method are not really satisfactory and should be improved about ten fold, *i.e.*, the sample treatment requires further attention.

TABLE III

DETECTION LIMITS AND RECOVERIES OF TRIORGANOTIN COMPOUNDS IN SPIKED SEDIMENTS AND SOILS

Organotin compounds were added to the dried sediments and soils, soxhlet extracted and determined by HPLC. Results are for triplicate determinations.

Compound	Added (μg/g)	Sediments		Soils	
		Recovery (%)	Detection limit[a] (μg/g)	Recovery (%)	Detection limit (μg/g)
TCT	2.6	125–130	3	95–100	0.3
FBTO	0.8	100–135	2	91–93	0.2
TPT	1.2	65–105	3	44–59	1

[a] Detection limits are calculated as worst-case example for Hertentocht sediment; detection limits for Maarsseveen sediment are similar to those for soil samples.

CONCLUSIONS

Normal-phase HPLC on a cyano-bonded column coupled on-line with post-column photoconversion and morin complexation allows the determination of low nanogram amounts of triorganotin compounds. In this work, all three organotin pesticides currently in use in agriculture (TPT, FBTO and TCT) were determined in one HPLC run for the first time. Detection limits in surface water are *ca.* 0.02 μg/l and, apart from liquid–liquid extraction and evaporation, no clean-up is required. This makes the method a valuable tool for water analysis. As an example, TPT was determined in surface water adjacent to a potato field that had been sprayed with this pesticide.

Because of fluorescent background interferences, with sediments and soils the detection limits are distinctly higher, *viz.* in the low μg/g range. For real samples these limits are too high and further optimization of the (extraction) procedure is required. For surface water samples the present HPLC–reaction detection technique offers a simple and fast determination method.

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