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Solid-Phase Extraction Combined with High-Performance Liquid Chromatography−Atmospheric Pressure Chemical Ionization−Mass Spectrometry Analysis of Pesticides in Water: Method Performance and Application in a Reconnaissance Survey of Residues in Drinking Water in Greater Cairo, Egypt

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Monitoring of water resources for pesticide residues is often needed to ensure that pesticide use does not adversely impact the quality of public water supplies or the environment. In many rural areas and throughout much of the developing world, monitoring is often constrained by lack of testing facilities; thus, collection of samples and shipment to centralized laboratories for analysis is required. The portability, ease of use, and potential to enhance analyte stability make solid-phase extraction (SPE) an attractive technique for handling water samples prior to their shipment. We describe performance of an SPE method targeting a structurally diverse mixture of 25 current-use pesticides and two common degradates in samples of raw and filtered drinking water collected in Greater Cairo, Egypt. SPE was completed in a field laboratory in Egypt, and cartridges were shipped to the United States for elution and high-performance liquid chromatography−atmospheric pressure chemical ionization−mass spectrometry analysis. Quantitative and reproducible recovery of 23 of 27 compounds (average = 96%; percent relative standard deviation = 21%) from matrix spikes (1 μg L^{-1} per component) prepared in the field and from deionized water fortified similarly in the analytical laboratory was obtained. Concurrent analysis of unspiked samples identified four parent compounds and one degradate in drinking water samples. No significant differences were observed between raw and filtered samples. Residue levels in all cases were below drinking water and "harm to aquatic-life" thresholds, indicating that human and ecological risks of pesticide contamination were relatively small; however, the study was limited in scale and scope. Further monitoring is needed to define spatial and temporal variation in residue concentrations. The study has demonstrated the feasibility of performing studies of this type using SPE to extract and preserve samples in the field. The approach should be broadly applicable in many settings.

KEYWORDS: Solid; phase; extraction; pesticide; monitoring; quality; control

INTRODUCTION

There is extensive literature that describes procedures for pesticide analysis of water (*1*, *2*). Successful use is often constrained by the need to store samples for variable periods of time prior to analysis and/or shipment of samples from remote sample collection sites to centralized testing facilities (*3*−*6*). This is the case in many rural areas in the United States and in much of the developing world. The portability, ease of use, and potential to enhance analyte stability makes solid-phase extraction (SPE) an attractive technique for handling water samples prior to their shipment.

Enhanced pesticide stability after SPE has been reported in numerous studies (*3*−*9*). In addition, the technique can be readily adapted for field use and SPE cartridges and filters typically weigh less than a few grams and are nonhazardous; thus, large numbers of samples can be shipped great distances at relatively low cost using common carriers.

When SPE is used, quantitative and reproducible recovery of target analytes from sample matrices must be demonstrated. The need for this is based on the fact that the physical and chemical properties of pesticides and adsorbents used in SPE devices vary widely. Development of a universal SPE adsorbent that will quantitatively recover all pesticides from water remains

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elusive (*7*, *10*, *11*). When SPE devices are stored or shipped, analyte stability must also be demonstrated. Studies have shown that the extent to which pesticide recoveries may be reduced through degradation after SPE was dependent on SPE adsorbent and pesticide properties, conditions under which SPE devices were stored after water extractions were performed, and the length of time between extraction and elution (*4*−*9*).

In this report, performance of an SPE procedure for multiresidue analysis of a structurally diverse mixture of current-use pesticides in water is described. SPE was performed in a field laboratory in Egypt, and cartridges were shipped to the United States for elution and high-performance liquid chromatography (HPLC)−atmospheric pressure chemical ionization (APCI)−mass spectrometry (MS) analysis. The method was used for a reconnaissance survey of residues of the target compounds in raw and filtered drinking water in Greater Cairo. The water source is the Nile River. Pesticide use for irrigated crop production in close proximity to the city is intense, and irrigation return flow is typically returned directly to the river through a series of drains and canals that are upstream of drinking water intakes; thus, pesticide contamination is a water quality concern (*12*, *13*). In one related study, relatively high levels (>10 μg L^{-1}) of organophosphate insecticides were reported in samples collected from ditches draining agricultural fields (*14*). To our knowledge, investigations that have focused on the drinking water supply are limited to a few unpublished results (*15*).

METHODS AND MATERIALS

Chemicals. Solvents were purchased from Fisher Scientific (Hampton, NH), formic acid and 2-chlorolepidine from Sigma-Aldrich (St. Louis, MO), and pesticide standards from Chem Service Inc. (West Chester, PA). The 27-component mixture used for spikes was prepared by dilution of primary standards in methanol in the analytical laboratory (**Table 1**). Aliquots of the mixture were retained by the laboratory for preparation of deionized water spikes and were shipped to Egypt for matrix spiking. Most of the compounds were active ingredients in current-use products and have been widely used for crop protection.

Water Samples. In September, October, and December, 2004, raw and filtered drinking water samples were collected at four water treatment facilities located on the banks of the Nile River in Greater Cairo, Egypt (**Figure 1**). At each facility, water was withdrawn from the Nile River directly into a large holding tank open to the atmosphere. The water was subsequently passed through a sand filter and stored in a second open tank before disinfection and distribution into the public water supply system (*16*). Water samples were collected directly from the tanks at a depth of 5 m below the surface using a Van Dorn sampler. Water from the sampler was used to fill two 1 L glass bottles. After collection, samples were chilled, transported to a field laboratory, and vacuum filtered. One of each of the two containers collected at each sample location during each sample event was then spiked with 1 mL of the pesticide spiking solution. The spiking level was 1 μg L^{-1} of each compound. All samples were stored in the dark in a refrigerator.

SPE. Within 3−5 days of sample collection, samples were drawn through an Oasis HLB SPE (6 mL; 0.2 g) cartridge (Waters Inc., Milford, MA) by vacuum using a vacuum manifold (Sigma-Aldrich). After this, cartridges were flushed with 2 × 10 mL aliquots of distilled−deionized water followed by reapplication of the vacuum for 15 min to remove residual water. Cartridges were then wrapped in aluminum foil and stored in a refrigerator. A laboratory blank prepared by SPE of 1 L of distilled−deionized water was included with each sample set. SPE cartridges were shipped using commercial international airmail service. They were received at the analytical laboratory in the United States in 5−6 days. Each shipment, which included 24 cartridges, weighed <454 g and cost approximately 200 Egyptian pounds ($40 U.S.). Upon receipt, cartridges were eluted sequentially with 3 mL each of methanol and methylene chloride. Combined eluents were concentrated to <1 mL by evaporation under a stream of N_2 gas and then adjusted to 1.25 mL (1 g) with methanol. Extracts were fortified with 5 μg of the internal standard, 2-chlorolepidine, and stored at −20 °C. Distilled−deionized water spikes (1 L) were prepared in the analytical laboratory using the same pesticide mixture. Immediately after SPE, cartridges were eluted and solvents were concentrated as described for drinking water samples.

Table 1. Target Compounds, HPLC Retention Time Data, and Full-Scan MS Ions and Relative Base Peak Response and Estimated MDL

compound	class[a]	peak[b]	RRT[c]	MS[d]	RRF[e]	MDL[f] (μg L^{-1})
DIA	chlorotriazine (M)	1	0.47	174	1.1	0.01
DEA	chlorotriazine (M)	2	0.62	188	1.7	0.01
prometon	triazine (H)	3	0.65	226	2.0	0.01
cyanazine	chlorotriazine (H)	4	0.76	241	1.5	0.01
ametryn	triazine (H)	5	0.78	228	2.6	0.01
metribuzin	triazine (H)	5	0.78	215	1.5	0.01
simazine	chlorotriazine (H)	6	0.79	202	0.62	0.01
tebuthiuron	phenylurea (H)	7	0.82	229	1.0	0.01
carbaryl	carbamate (I)	8	0.84	202	0.62	0.01
fluometuron	phenylurea (H)	9	0.88	233	0.78	0.01
atrazine	chlorotriazine (H)	10	0.91	216	2.2	0.01
metalaxyl	miscellaneous (F)	10	0.92	280	3.0	0.01
diuron	phenylurea (H)	11	0.95	233	0.36	0.01
norflurazon	phenylurea (H)	11	0.96	304	2.6	0.01
2-chlorolepidine	internal standard	12	1.00	178	1.0	
methylparathion	organophosphate (I)	12	1.01	234	0.06	0.1
malathion	organophosphate (I)	13	1.05	331	1.5	0.01
ethoprop	organophosphate (I)	14	1.10	243	1.7	0.01
acetochlor	acetanilide (H)	14	1.10	224	0.84	0.01
alachlor	acetanilide (H)	14	1.11	238	1.0	0.01
metolachlor	acetanilide (H)	15	1.11	284	2.5	0.01
diazinon	organophosphate (I)	16	1.18	305	1.9	0.01
oxadiazon	miscellaneous (H)	17	1.32	345	0.13	0.1
ethalfluralin	dinitroaniline (H)	18	1.35	300	0.04	0.1
chlorpyrifos	organophosphate (I)	19	1.37	350	0.43	0.01
pendimethalin	dinitroaniline (H)	20	1.39	282	0.66	0.01
trifluralin	dinitroaniline (H)	21	1.41	302	0.04	0.1
tribufos	miscellaneous (D)	22	1.47	315	2.5	0.01

[a] Ref *35*; M, metabolite; H, herbicide; I, insecticide; F, fungicide; and D, defoliant. [b] **Figure 2**. [c] RRT, relative retention to the internal standard. [d] Base peak in full-scan MS. [e] RRF, relative response factor to the internal standard. [f] MDL, method detection limits based on SPE of a 1-L water sample.

HPLC-MS. Extracts were analyzed with a Thermoquest LCQ DECA system using the instrument's APCI interface (Thermoquest-Finnigan, San Jose, CA). HPLC separations were performed on a 150 mm × 4.6 mm i.d. stainless steel Gemini column packed with 5 μ C_{18}-silica, 110 A (Phenomenex, Torrence, CA) using 0.1% formic acid (A) and methanol (B) gradient elution. Initial conditions, 90% A and 10% B, were changed linearly to 10% A and 90% B in 24 min when the mass flow rate was decreased from 1.0 to 0.5 mL min^{-1} in 1 min. Conditions were held isocratic until 27 min when flow was returned linearly to 1 mL min^{-1} in 1 min. At 30 min, the mobile phase composition was returned linearly to initial conditions in 1 min. Prior to each use, the mass spectrometer response was optimized by "autotune" for the $(M + H)^+$ ion produced during infusion of 10 μg mL^{-1} solution of malathion in methanol. Vaporizer and capillary temperatures were 450 and 180 °C, respectively, and N_2 sheath and auxiliary gas flows were set to provide maximum $(M + H)^+$ response. During each MS analysis, the ion-trap mass filter was scanned from $m/z^+ = 150$ to 400. Base peaks of spectra were used for quantitation. Four point calibrations, over the concentration range 0.01−10.0 μg mL^{-1}, were made ($r^2 > 0.999$). Confirmation and quantitation of analytes detected in unspiked samples were by collision-induced dissociation (CID) in the MS^2 mode. The relative fragmentation energy was determined during infusions by software-controlled optimization. In all cases, $(M + H)^+$ was the precursor ion and the product monitored for quantitation was the base peak in the MS^2 spectrum. For quantitation, four point calibrations, over the concentration range 0.001−1.0 μg mL^{-1}, were made ($r^2 > 0.999$).

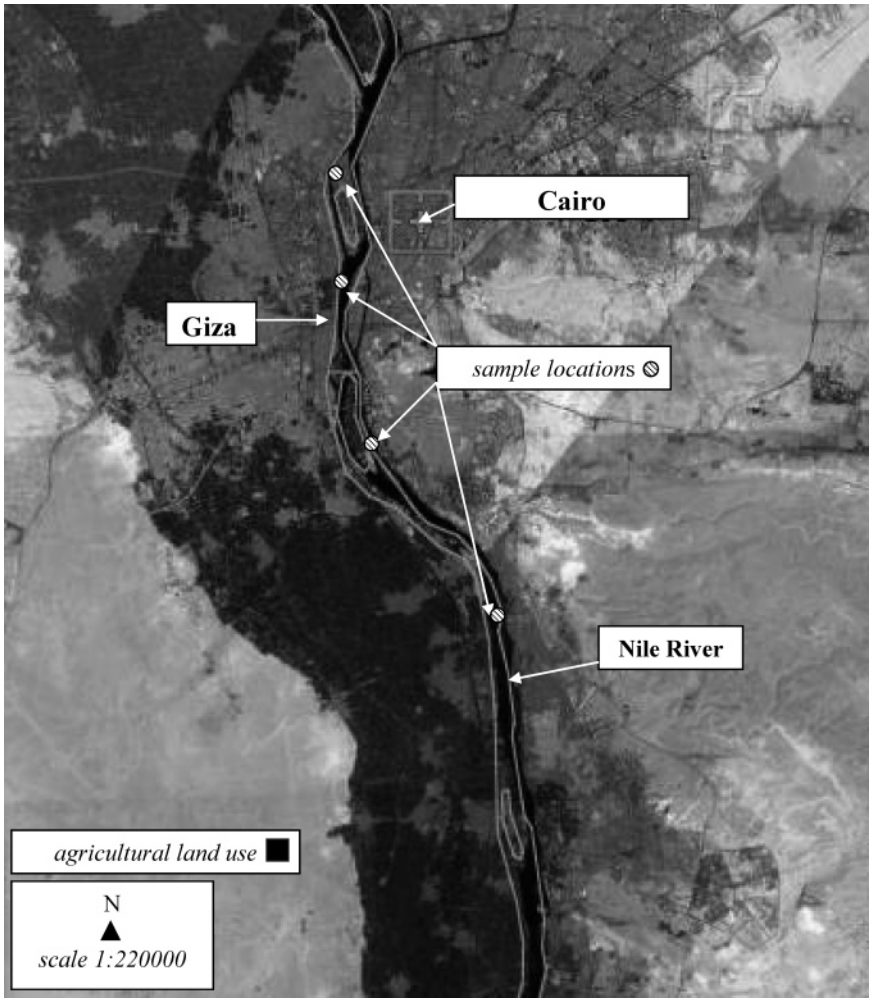

Figure 1. Location of water sample collection sites at drinking water withdrawal and treatment facilities in Greater Cairo, Egypt (base map ref *36*).

RESULTS AND DISCUSSION

HPLC-MS Method Development. MS spectra of each compound were obtained by infusion of single component (10 μg mL^{-1} in methanol) standards using a syringe pump. Base peaks corresponded to $(M + H)^+$ with the exception of trifluralin, ethalfluralin, methylparathion, alachlor, and acetochlor (**Table 1**). Base peaks of these compounds were produced by neutral losses including NO from methylparathion, H_2O_2 from ethalfluralin and trifluralin, CH_3O from alachlor, and from acetochlor, CH_3CH_2O. Using MS base peaks for detection, HPLC conditions for the mixture were evaluated.

Final conditions reflected a progressive decrease in the binary linear gradient rate until "baseline" separation of simazine and carbaryl was achieved. This was done since base peaks of both were $(M + H)^+ = 202$; thus, their detection (using base peaks) required chromatographic separation. Conditions yielded 22 peaks for the 27-component mixture (**Figure 2** and **Table 1**). There were five groups of co- or partially coeluting compounds. In each case, specific identification of all compounds was possible on the basis of base peaks since compounds produced unique ions. One of the compound groups that coeluted included alachlor and acetochlor. These compounds have identical molecular formulae and nearly identical structures. However, their base peaks, which were produced by neutral losses-associated cleavage of terminal alkoxy groups, were unique since this is a point where compound structures differ. To assess potential matrix effects on MS response of compounds that coeluted, responses of the compounds were evaluated by comparing single component injections to the mixture. Total area counts in all cases differed by <5%.

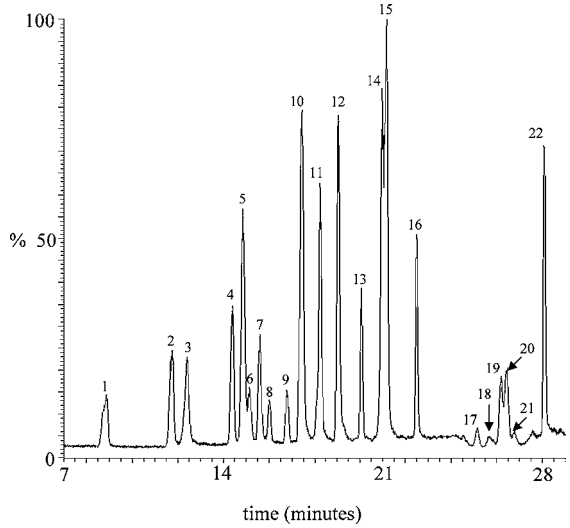

Figure 2. Total ion current chromatogram of pesticide spiking mixture (peak labels **Table 1**).

One other factor taken into account in selection of HPLC conditions was flow adjustment to enhance the chlorpyrifos signal. By reducing flow from 1.0 to 0.5 mL min^{-1} during the

Table 2. Percent Recovery of Target Compounds by SPE from Distilled–Deionized Water and Raw and Filtered Drinking Water Samples

	distilled–deionized water ($n = 3$)		drinking water ($n = 24$)	
compound	average	RSD	average	RSD
acetochlor	95	8	86	22
alachlor	100	8	87	21
ametryn	88	11	89	21
atrazine	95	9	92	14
carbaryl	94	8	110	20
chlorpyrifos	104	8	94	25
cyanazine	92	10	110	13
DEA	95	11	100	11
DIA	100	11	100	11
diazinon	94	10	89	31
diuron	98	8	110	13
ethalfluralin	79	12	63[a]	72
ethoprop	94	7	94	31
fluometuron	94	8	100	16
malathion	99	8	104	21
methylparathion	91	6	81	51
metalaxyl	98	9	110	14
metolachlor	93	9	95	18
metribuzin	91	9	94	12
norflurazon	96	7	100	11
oxadiazon	130	6	110	20
pendimethalin	85	9	69	25
prometon	98	11	100	24
simazine	96	11	94	14
tebuthiuron	92	9	110	12
tribufos	85	11	78	19
trifluralin	81	11	59[a]	85

[a] Eight samples < MDL; inserted % recovery (10%) based on MDL (0.1 μg L^{-1}).

time when the compound eluted, the base peak response ($m/z^+ = 350$) was increased 10 times. The motivation to change the flow to increase the signal was based on Asperger et al. (*18*). While flow programming substantially increased the chlorpyrifos signal, there was ≈2 times decrease in the response of other closely eluting compounds (ethalfluralin, pendimethalin, and trifluralin).

Among all compounds, relative response factors (RRF) to the internal standard were generally within a factor of 3 (**Table 1**). This was indicative of relatively uniform and sensitive MS response. Method detection limits (MDLs) based on the lowest concentration standard used in calibrations and SPE of 1 L of water were typically 0.01 μg L^{-1} (**Table 1**). The signal-to-noise for the 0.01 μg mL^{-1} solution was typically >100 to 1. Exceptions were trifluralin, ethalfluralin, oxadiazon, and methyl-parathion. These compounds had relatively low RRFs, and estimated MDLs were 10-fold greater. Relatively poor trifluralin and methyl-parathion APCI-MS response has been reported previously (*18*, *19*).

SPE Performance. Recoveries of the compounds from distilled−deionized water spiked in the analytical laboratory and processed immediately by SPE averaged 79−130%, while matrix spikes recoveries averaged 63−110% (**Tables 2** and **3**). When compared by compound, differences between average recoveries from the two water types were generally small, 0−18%, and in no case were means significantly different ($P = 0.05$; *t*-test). However, data did indicate a trend to lower average recovery and higher percent relative standard deviation (RSD) for some compounds in matrix spikes. The largest differences were for the dinitroanilines, pendimethalin, ethalfluralin, and trifluralin, and the organophosphate, methylparathion. Ethalfluralin, trifluralin, and methylparathion average recoveries were also the most variable among all analytes with RSDs ranging from 51 to 85%. The range for all other compounds was 11−31%. Low recovery and/or large variation in these compounds were related to their low relatively APCI response and the fact that the spiking level (1 μg L^{-1}) was relatively close to MDLs of these compounds. Thus, the measurement uncertainty impact was likely amplified.

Table 3. Summary Statistics for Pesticide Detections in Drinking Water Samples Collected in Greater Cairo, Egypt[a]

	μg L^{-1}			
pesticide/ sample type	maximum	minimum	% detects	median (μg L^{-1})
atrazine ($m/z^+ = 174$)[b]				
raw	0.07	<0.001	92	0.005
filtered	0.006	<0.001	92	0.005
DEA ($m/z^+ = 146$)				
raw	0.08	<0.001	75	0.003
filtered	0.004	<0.001	50	0.001
diazinon ($m/z^+ = 169$)				
raw	0.03	<0.001	42	<0.001
filtered	0.04	<0.001	33	<0.001
malathion ($m/z^+ = 285$)				
raw	0.04	<0.001	58	0.006
filtered	0.06	<0.001	58	0.006
tribufos ($m/z^+ = 257$)				
raw	0.06	<0.001	100	0.02
filtered	0.05	<0.001	92	0.02

[a] Location: **Figure 1**; dates of collections: September, 25, October 13, and December 26, 2004; number of samples, 12 each (raw and filtered). [b] MS^2 product ions indicated in parenthesis were used for quantitation.

Data also indicated a potential for a "matrix effect", i.e., ionization suppression of the compounds due to coeluting salts or humic materials derived from water samples. Matrix-associated signal suppression was also indicated for the other dinitroaniline herbicide tested, pendimethalin. The average recovery from deionized water spikes was 16% greater than from matrix spikes. Matrix effects have been reported for various analytes in HPLC-APCI-MS; however, signal enhancement rather than reduction is most commonly observed (*20*−*22*). Given this, it appears that further work is needed to confirm whether or not the matrix may have reduced compound responses described. It is notable that for carbaryl, cyanazine, diuron, metalaxyl, oxadiazon, and tebuthiuron, a modest ≈10% (difference between average recovery of deionized water and matrix spikes) signal enhancement was indicated.

Another possible explanation of the lower recoveries in matrix when compared to deionized water spikes was analyte degradation while sorbed on SPE cartridges during storage shipment. Possible mechanisms include both abiotic and microbially mediated hydrolysis and oxidation. Although this was possible, degradation did not appear to explain the relatively low recoveries observed for the three dinitroaniline herbicides and methylparathion. This conclusion is based on the fact that recoveries of another organophosphate, malathion, and the carbamate, carbaryl, were not significantly different ($P = 0.01$) from 100% in matrix spikes. If hydrolysis and/or microbial degradation had occurred, recovery of these compounds would likely have been strongly impacted since their hydrolysis and aerobic biodegradation half-lives are relatively short when compared to other targeted compounds (*23*, *24*). For example, the value commonly reported for malathion hydrolysis half-life in water at neutral pH is 6 days. The time between SPE of samples in the field laboratory and receipt and elution of the

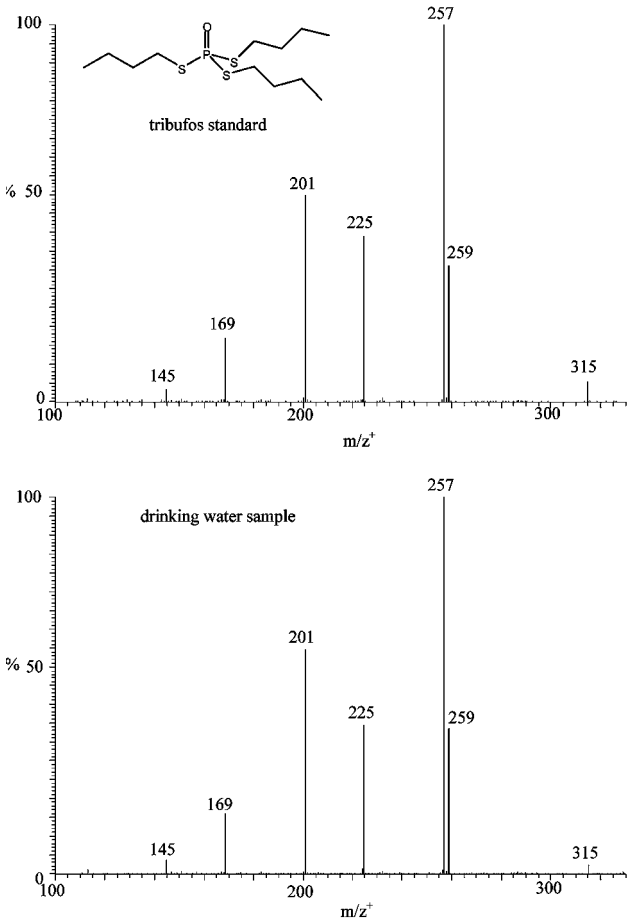

Figure 3. MS^2 spectra of tribufos analytical standard and spectra of the corresponding peak detected in the chromatogram in the water sample extract. The precursor ion was $m/z^+ = 315$.

SPE cartridges in the analytical laboratory was typically 8−10 days; thus, malathion recovery would have been reduced by 50% or more if compounds on SPE cartridges were subject to hydrolysis. It is likely that failure to observe hydrolysis was due to very low water retention on the cartridges after SPE. In a prior study, we found that differences in SPE cartridge weights before and after extraction were <0.01 g when cartridges handled similarly (*25*). Low water retention and relatively high recovery of a wide range of compounds even after flushing cartridges with air was identified as an advantage of the polymeric sorbents used in our study over silica-based sorbents (*11*).

In sum, with few exceptions (four of 27 compounds), quantitative recovery of the target analytes was achieved. This is consistent with several published reports describing use of the same sorbent material, Oasis HLB, in both off- and on-line SPE (*25*−*28*). Recovery data also indicated that most compounds were stable after sorption on cartridges. Periods of storage and shipment were 8−10 days.

Residues in Water Samples. MS data indicated detection of five target compounds, DEA, atrazine, diazinon, malathion, and tribufos, in one or more of the unspiked samples. CID analyses confirmed results (**Table 3**) and provided a 10-fold lower limit of detection. None of these or other target compounds were detected in blanks prepared for each sample shipment ($n = 3$) indicating a relatively low potential for false-positive results. Notably, both carbaryl and chlorpyrifos were <MDL (0.01 μg L^{-1}) in all samples ($n = 24$). In a previously published study, these compounds were found at relatively high levels (13−50 μg L^{-1}) in water samples that were collected from canals and drains that discharge to the Nile at points upstream of drinking water treatment plant intakes (*14*).

For both raw and filtered samples, the decreasing trend in frequency of detection (%) was tribufos > atrazine > DEA > malathion > diazinon. The corresponding trend in median concentration was tribufos > malathion > atrazine > DEA > diazinon. Furthermore, no statistically significantly difference in medians ($P = 0.1$; Wilcoxon sign rank test) was observed when raw and filtered samples were compared by analyte. Thus, data did not indicate that the filtration system has the potential to remove relatively low levels of these compounds from the raw river water.

Detection of DEA, atrazine, diazinon, and malathion in samples was consistent with their detection in rivers and streams in other settings. For example, during the National Water Quality Assessment Program (NAWQA) conducted by the U.S. Geological Survey during the 1990s in the United States, these compounds were among the most frequently detected in rivers, streams, and shallow groundwater (*17*). Detection frequencies in our samples were comparable ranging from 33 to 100% depending on the compound and water source. Concentrations were also generally low with medians in all cases ≤0.02 μg L^{-1} and maxima (**Table 3**) below established drinking water contaminant thresholds and water quality criteria for protection aquatic life (*17*, *29*). The relatively low pesticide concentration in samples likely reflected the fact that the Nile River drainage basin above Cairo and the river's discharge are among the largest in the world (*30*). Generally, pesticide concentrations in samples collected from streams and rivers tend to decrease as the drainage basin size and discharge are increased (*17*).

Among all compounds, tribufos was the most frequently detected and had the highest median concentration in both raw and filtered samples. As noted, the compound was not detected in blanks prepared and shipped with each sample set. There was also a very close match in HPLC retention times, MS, and MS^2 spectra of peaks detected in sample extracts with respect to tribufos analytical standards. Agreement in MS^2 spectra data is shown for a sample extract and a standard in **Figure 3**.

Data indicated that tribufos was present in Cairo's water supply and that it was being used in the Nile River watershed at points where it has the potential to reach the sampling points (**Figure 1**). The compound is the active ingredient in products used to chemically defoliate cotton (*31*). Cotton is a significant commodity in Egypt contributing ≈1% of world production (*32*).

A risk assessment conducted by the U.S. Environmental Protection Agency reported that there were no available surface water quality data for tribufos in the United States (*31*). Given this, the extent to which the compound occurs in surface water in cotton-producing areas in the United States and other use regions is unknown. Published studies under conditions in the United States have indicated that a substantial amount of the product may be entrained in runoff from treated fields (*31*, *33*, *34*). Drift and/or vapor deposition also appear to be transport pathways to surface water, which should be considered (*31*).

ABBREVIATIONS USED

APCI, atmospheric pressure chemical ionization; HPLC, high-performance liquid chromatography; MDL, method detection limit; RSD, percent relative standard deviation; and SPE, solid-phase extraction.

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