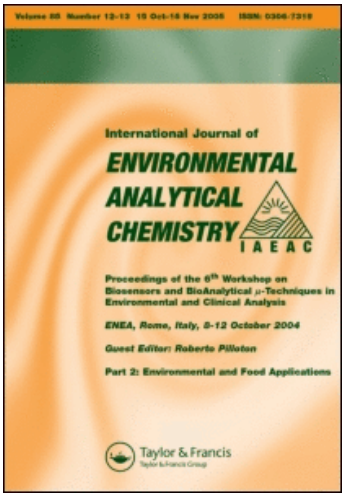

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EXAMINATION OF SURFACE WATER SAMPLES USING GAS CHROMATOGRAPHY-ATOMIC EMISSION DETECTION

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In two separate pesticide monitoring studies, surface water samples were collected from different locations in southern Ontario. Following clean up, the extracts were initially analyzed for selected P-containing pesticides using capillary column GC equipped with N/P and ECD detectors. These extracts were subsequently analyzed by GC-AED for C-, S-, N-, P- and O-containing compounds. All target compounds identified by GC-NPD/ECD analysis were detected using the GC-AED technique. Concentrations of the target compounds were comparable as calculated from the results of both methods of analysis. Additional non-target compounds containing S and N were identified in the samples. The peaks were collated with respect to retention time and response. One of these compounds, benzothiazole, was found in 27 of the 34 samples.

KEY WORDS: Atomic emission detection, pesticides, water, benzothiazole.

INTRODUCTION

Creeks and streams transport surface water from micro drainage areas into larger receiving bodies such as lakes. Chemicals found in the waters of creeks, in part, reflect human activities in the areas that the creeks drain. The types and amounts of the chemicals should depend on the degree of urbanization and agricultural activities in the drainage area. Two types of considerations were of particular interest. The first was the presence of organic chemicals in surface waters flowing through agricultural areas after pesticide application. The second was the occurrence of organics in surface waters draining urban areas after precipitation events. This latter subject has been the topic of other studies. One such study[1] investigated gross parameters such as major ions and flow variation of a small drainage area in Kansas. Another study conducted in California[2] included organics in the runoff water but limited the investigation to particular pesticides. Other studies[e.g. 3] have been conducted whose results and conclusions combined with the others cited, lead to a better understanding of the transport of chemicals and the runoff process. Considerable efforts have been expanded to the investigation of agricultural chemicals in surface water, all too numerous to cite. An earlier paper investigated the presence of 2,4-dichlorophenoxyacetic acid (2,4-D) in flowing waters which were far removed from the application area[4]. Indeed the analysis of

pesticide residues is of major importance in research[5] as well as in monitoring[6]. One thrust of the present study is to analyze samples collected from urban runoff and from agricultural activities by gas chromatography to determine if the diverse samples contain a type of chemical signature dependent on the sample type and area from which it was collected.

Investigations of surface water samples by gas chromatographic techniques invariably involve target compound analysis[7] which utilizes only a small fraction of the information available from the chromatograms. This occurs for several dependent reasons. Surface water samples contain a large number of organic compounds and this produces complex chromatograms of the extracts as analyzed by GC detectors like the FID or ECD. These detectors measure some structural feature of the eluting compounds. Other than identifying known peaks from anticipated retention times derived from results from two dissimilar columns, the remaining information is often very difficult to interpret. The MS detector can provide more detailed information as to probable structure of some peaks, but the identification of many eluants, especially when coelutants are present, is difficult. Using an automated GC-atomic emission detector (AED)[8,9], examination and interpretation of the chromatograms from such complex mixtures can be facilitated by examining the element specific heteroatom chromatograms[10,11].

With atomic emission detection, analysis of the column effluent is element specific, as there is generally no interference from other elements. As almost all compounds eluting from a chromatographic column contain carbon, the carbon chromatogram would be similar in pattern to an FID or MSD chromatogram. Consideration of only the heteroatoms such as S or N, provides a simplified approach to the task of interpreting the resulting chromatograms as there are fewer compounds containing these elements than there are with only C and H. With fewer peaks to consider, correlation between the results from diverse samples or over time is simplified. In addition, since the elemental responses are generally transparent to the responses from other elements, some problems related to coelution are minimized. Therefore compound A which does not contain element S may coelute with compound B which does contain hetero-element S. The carbon response would reflect the coelution, but the S response would only be dependent on the amount of compound B. Therefore the concentration of the target compounds can be determined from the response of the heteroatom. The presence of heteroatom containing target compounds can be confirmed by the retention time of the carbon and heteroatom peaks on a single column although some care is necessary. When a compound contains more than one heteroatom and is present in detectable concentrations, its presence and concentration can be determined with greater accuracy. If the eluate is not a target compound, information is available to partially assign a structure to the compound. The instrumental response of the eluting compound for each of the elements analyzed for can be used to determine the relative number of each heteroatom present in the molecule. If the analogous carbon peak is free of interferences the basic structure of the eluting compound can be calculated. The more heteroatoms present in a compound the more information is provided to the analyst.

The first set of samples of surface water were collected after pesticide application in agricultural areas. The second set were from urban runoff collected after precipitation events. Common pesticides were first identified and quantified by target compound analysis using GC-NPD/ECD/MSD. A manuscript of this method is currently in preparation, and since the details of the method are not available in the literature, details of it are reported here. The current study was not undertaken to compare the two methods of detection, but to examine the aqueous samples for hetero-atom-containing non-target compounds. Our approach was to consider the ECD/NPD results as being

acceptable as it was developed specifically to analyze for the P-containing pesticides listed in the method section. Initially the GC-AED's capability to detect the target compounds was compared to the results from the ECD/NPD method. The next step was to compare the concentrations of the target compounds identified by the two methods. Finally the samples were examined for other compounds containing heteroatoms (S, N, P) by the GC-AED.

METHODS

Samples related to pesticide application were collected from two agricultural areas in southern Ontario. One was from the Holland Marsh, area, north of Toronto, where root crops are prevalent. The other area was in the Niagara Peninsula where the cash crop is fruit production. For the urban runoff study, two other areas were sampled. One of these, near Guelph, Ontario, contained two storm water detention ponds located in separate subdividisons. Appropriate control samples were also taken prior to events. The other are was the Hamilton Harbour watershed. In this area, streams flowing into the harbour were sampled at locations where the receiving water in the bay did not influence the water in the creeks. One site was on Red Hill Creek, collected 1 km from the bay, another was in Indian Creek (0.5 km), another was Spencer Creek (2 km) and the last was Grindstone Creek (2 km). Each micro watershed drained areas with different degrees of urbanization. Samples were taken before and after precipitation events (1 to 3 hours after the event which coincides with maximum flow). For each study, grab samples of 1 L were collected from under the surface in glass bottles, then placed in an ice containing container to be returned to the laboratory. Immediately on returning to the laboratory, 100 mL of dichloromethane (DCM) was added to each sample and the sample shaken, then stored in the dark at 4°C until extraction. Within 48 hr. after collection, an additional 100 mL DCM was added to each sample and the sample shaken for 2 min., with the DCM being collected into a round bottom flask after phase separation. Then the aqueous solution was extracted 2X 70 mL DCM and the DCM extracts combined. The DCM was dried by passing through anhydrous Na_2SO_4 contained un an Allihn filter. After adding 3 mL isooctane, the DCM solution was reduced to 2–3 mL and transferred to a 15 mL centrifuge tube washing with 2 × 2 mL hexane. Reduction of the volume to 1 mL is achieved by heating the mixture to 38°C and passing N2 over the solvent surface. The concentrate is added to a column containing 10 g of deactivated silica (10%) topped with 0.5 g of anhydrous Na_2SO_4 and previously washed with 50 mL hexane. The sample is eluted with 75 mL DCM. The eluant is combined with 3 mL of isooctane and the volume is reduced to 2 mL on a roto-evaporator. Then the sample is transferred to a 15 mL centrifuge tube rinsing with 2X 3 mL of hexane. The contents of the tube are reduced to 1 mL by heating to 38°C and passing a stream of N_2 over the solvent surface. This is the final solution used for GC analysis which is stored in the dark at 4°C until needed for analysis.

For the GC-NPD/ECD analysis, a 3 uL injection was split evenly between a DB-5 and a SP-608 column. Each column was 30 m × 0.25 mm with a 0.025 u liquid phase. The DB-5 column eluted into an EC detector (350°C) while the SP-608 column was attached to a NP detector (320°C). Each injection was delivered by an automatic sampler and the injector, set at 250°C, was operated in the splitless mode, which had a purge delay of 30 sec. The initial oven temperature of the HP5980 gas chromatograph was set at 80°C for 2 min., then the temperature increased at 10°C/min. until 160°C and this temperature held for 1 min. after which the temperature was increased at 3°C/min. until 265°C was

reached and this temperature was maintained for 15 min. The carrier gas was He with column head pressure of 15 psi. Confirmation was performed using an Hp 5970 MSD. The chromatographic conditions was the same as for the ECD/NPD analysis and an DB-5 capillary column with dimensions similar to that used for the ECD/NPD analysis.

Natural water samples and ion-exchanged distilled water were spiked with standards at two concentrations ranges of 100 ng/L and 100 ug/L. Using the extraction procedure outlined above, recoveries were measured at 80 to 100%.

For CG-AED analysis, the HP 5921A atomic emission detector was used in tandem with an HP5890B GC which was equipped with an automatic sampler. All operating conditions were controlled by the HP AED Pascal workstation. The elements C, N, S, O and P were measured by recording the emission lines at 193.5, 174.3, 181.3, 777 and 171 nm, respectively. As various dopant gases were used for the different elements (H_2 and O_2 for C, N, and S; H_2 for P; and H_2 with N_2/Ch_4 for O_2) and the photodiode array covered the range of 250 nm, 3 injections were required for each sample with each using the same temperature program on the gas chromatograph. The initial temperature of 90°C was maintained for 2 min. then increase at a rate of 30°C/min. until 200°C at which time the rate was decreased to 6°C/min. until the temperature reached 255°C and this temperature was maintained for 10 min. The solvent for all samples and standards was isooctane and injection volumes of 1 uL were made in the splitless mode. A SE52-XL column, 30 m × 0.25 mm id, with a film thickness of 0.25 u was supplied by Hiresco (Mississauga, Ont.). The solvent is vented during the interval of 1.3 to 3.8 min., otherwise it would extinguish the plasma. The transfer line temperature between the GC and detector was maintained at 260°C and the cavity temperature was 265°C. The carrier gas flow rate was 4.5 mL/min.

Primary AED standards were contained in three separate solutions. The compounds used for this purpose are as follows with the solution number containing that compound denoted by the number: phorate(1) ($C_7H_{17}O_2SP$), dimethoate(1,2) ($C_5H_{12}O_3S_2NP$), diazinon(1) ($C_{12}H_{21}O_3SN_2P$), ronnel(1) ($C_8H_8O_3SPCl_3$), phosphamidon(3) ($C_{10}H_{19}O_5PNCl$), methylparathion(1) ($C_8H_{10}O_5SNP$), parathion(1) ($C_{10}H_{14}O_5SNP$), cruformate(1) ($C_{12}H_{19}O_2PNCl$), ethion(1) ($C_9H_{22}O_4S_4P_2$), phosmet(2) ($C_{11}H_{12}O_4S_2NP$), malathion(2,3) ($C_{10}H_{19}O_6S_2P$), azinphosethyl(2) ($C_{12}H_{16}O_3S_2N_3P$), azinphosmethyl(2) ($C_{10}H_{12}O_3S_2N_3P$), butylate(3) ($C_{11}H_{19}OSN$), diallate(3) ($C_{10}H_{17}OSNCl_2$), triallate(3) ($C_{10}H_{16}OSNCl_3$), metribuzin(3) ($C_8H_{14}OSN$), α-endosulphan(3) and β-endosulphan(3) ($C_9H_6O_3SCl_6$). Each compound was present in its solution at the concentration of 1 ng/uL. The standard solution for the ECD/NPD method contained dibrom, phorate, dimethoate, terbufos, fonofos, diazinon, disulfoton, malathion, chlorpyrifos, parathion, ethion, phosmet and azinophsomethyl. Chemicals not contained in the AED standard solutions were analyzed individually using the AED. Aliquots of standard solutions 1, 2 and 3 were analyzed before, during and after the analysis of the samples. The areas and retention times of the standard compounds were found to be consistant during the period required to analyze the samples. The concentrations of the target compounds in the samples were calculated from the area responses of the chemicals in the standards. These calculations were made using only the S-channel results. In previous studies, it was found that the reproducibility of results from the P-channel at low concentrations (about 10 pg) was poor as was the linearity of the response (11). Enhancing the P-response reproducibility by increasing the make-up gas flow rate produces a decrease in the minimal detectability caused by the dilution effect of the increased amount of gas present. The concentrations of benzothiazole were calculated from the S, N, and C responses of butylate as an authentic sample of this compound was not obtained until after all water extract samples had been analyzed. To ensure the calculated concentration values were reasonable, the responses of benzothiazole were calibrated against those of freshly analyzed butylate.

RESULTS

Both agricultural and runoff samples had been previously analyzed by GC-NPD/ECD with confirmation by GC-MSD. The results from the sample set related to agricultural pesticide application are shown in Table 1a. The prominent target compounds identified by the GC-NPD/ECD method were fonofos, chlorpyrifos, diazinon, and azinphosmethyl, with terbufos, malathion and ethion being present in two samples. The GC-AED technique identified diazinon, azinophosmethyl and ethion in the same samples. A temperature program used for screening many other samples from various origins (e.g. tainted fuels, tire fires, tire leachates) was used for this series of analyses as the retention times and responses of 21 standard compounds were reproducibly known. However, fonofos, diazinon and chlorpyrifos eluted at 10.00 min. ± 0.05 min. with this temperature program. Therefore the initial entries in Table 1(a) have no AED result with compare to the NPD/ECD results, although small peaks were observed in the element specific S and P chromatograms. Those samples containing ethion and azinophosmethyl exhibited reasonable agreement between the results from the NPD/ECD technique and the AED technique. The compounds detected in these latter samples were those contained in the standard solutions used for AED calibrations. To enhance the instrumental sensitivity to N, all fittings were changed on the GC-AED and it was recalibrated with the carrier gas flow rate being slightly altered after the agricultural application samples were analyzed.

The urban pesticide run-off samples were then analyzed as were three additional pesticide application samples. These results are contained in Table 1(b) as are the NPD/ECD method results. For only one of the 16 samples analyzed, the NPD/ECD method detected diazinon but the AED method did not. No target compounds were detected in 5 samples by either method. Of the other 14 positive identifications, the concentration values were within a factor of 2 for 9 compounds, the concentrations for two other compounds were determined to be within a factor of 3, and the concentrations of the other 3 compounds were within a factor of 7. There is a reasonable agreement between the NPD/ECD and the AED results, first with respect to the identify of compounds in the samples and second with respect to their concentrations. The differences in the concentration values determined by the two methods is not systematic, where one set of values is consistently higher or lower than the other, often caused by a faulty calibration standard. The nonsystematic differences observed here can be caused by coelutions or interferences.

Table 2 lists the compounds detected by the GC-AED, but not analyzed for by the NPD/ECD method. With the GC-AED technique, other heteroatom containing pesticides were identified. The chromatograms of several samples had a S-peak eluting at the same time as metribuzin. In the agricultural pesticide application samples, dimethoate was identified in three of the samples. These compounds were so identified on the basis of the retention times of the S response contained in the eluting compounds. Some of these compounds contain two heteroatoms (S, P, and/or N) such as parathion which contains both S and P. However at the low concentrations, the P response may or may not appear, and at these concentrations, as stated before, the response is not linear. The AED is not as sensitive for N as it is for S or P, and at low concentrations a signal for this element would not be expected. The concentrations of the compounds listed in Table 2 were determined from the S response.

Minimal detectable concentrations for each chemical is dependent on the amount of the element in the compound and the sensitivity of the detector to the element. Other factors, such as thermal stability of the compound in the injector and column, and active sites, will also influence the elemental response. Using the temperature program described for the AED, the minimal detectable amounts of S, N and P were 5, 40 and

Table 1 (a) Compounds identified in agricultural samples by GC-NPD/ECD and GC-AED (ng/L).

Samples #	*Location*	*Compound*	*NPD/ECD*	*AED (S-channel*
2902	HM	fonofos	74	86
		malathion	38	23
4173	HM	fonofos	191	–
4174	HM	chlorpyrifos	65	50
5030	HM	chlorpyrifos	105	–
5820	HM	terbufos	30	–
		chlorpyrifos	40	–
6272	HM	fonofos	26	–
		diazinon	101	–
6890	HM	fonofos	63	–
		diazinon	132	–
6892	HM	fonofos	27	–
		diazinon	115	–
6984	HM	diazinon	93	99
8453	HM	diazinon	81	109
8454	HM	azinphosmethyl	210	–
8456	HM	fonofos	53	–
		diazinon	20	70
3053	HM	ethion	2062	1700
4566	NP	azinphosmethyl	3122	3370
4567	NP	azinphosmethyl	–	2450
4568	NP	azinphosmethyl	182	150

HM = Holland Marsh NP = Niagara Peninsula

Table 1 (b) Compounds identified in runoff samples by GC-NPD/ECD and GC-AED (ng/L).

Samples #	*Location*	*Compound*	*NPD/ECD*	*AED (S-channel)*
2050	G-WP	diazinon	373	1000
4901	G-WP	diazinon	646	1010
8457	G-WP	dimethoate	1405	910
		diazinon	1584	1300
4902	G-DP	diazinon	474	855
2051	HH-SC	diazinon	112	705
2054	HH-RHC	dimethoate	1903	1415
		diazinon	130	620
7933	HH-RHC	diazinon	317	121
2912	HH-IC	dimethoate	272	370
		diazinon	91	432
2916	HH-IC	dimethoate	159	160
		diazinon	354	400
2046, 2042, 2034, 4176	HH-IC			
2915	HH-GC	diazinon	219	265
3397	HH-GC	diazinon	282	–
2045	HH-GC			

G – Guelph: WP = wet pond, DP = dry pond. HH = Hamilton Harbour:IC = Indian Creek, GC = Grindstone Creek, RHC = Red Hill Creek, SC = Spencer Creek

5 pg. In the specifications for the instrument, the manufacturers quote minimal detectable amounts as pg/sec, a term dependent on peak width. The temperature program described for the GC-AED produces well-shaped peaks, whereas that described for the ECD/NPD method takes longer than that used for the AED and the individual peaks are wider. At

Table 2 Other compounds identified in samples using GC-AED technique (ng/L).

(a) Urban runoff samples			*(b) Agricultural samples*		
Sample No.	*Compound*	*Concentration (ng/L)*	*Sample*	*Compound*	*Comcentration (ng/L)*
2050	diallate	150	2902	parathion	20
	metribuzin	125		ethion	50
2051	metribuzin	450	5030	parathion	160
2054	diallate	20		ethion	88
	metribuzin	p	5820	diazininon	70
2912	metribuzin	445		ethion	35
	malathion	370	6272	diallate	811
2915	ronnel	p		parathion	350
3397	butylate	85		ethion	210
	metribuzin	185	6890	dimethoate	150
	malathion	32	6894	dimethoate	52
4901	diallate	135	8453	dimethoate	100
	metribuzin	465	8456	dimethoate	53
4902	metribuzin	465	4567	α-endosulphan	80
3053	diazinon	665		β-endosulphan	51
	parathion	100			

low concentrations, there is a lowering of detectability for the AED instrument when the ECD/NPD temperature program was used on the AED.

Figure 1 illustrates the element specific (ES) S, P, and N chromatograms for one of the standard solutions used for calibrations. The first peak in the ES-S chromatogram is for phorate as it is in the ES-P chromatogram. As this compound contains no N, no ES-N peak was observed. The same is true for ronnel and ethion. In this figure, the N results were enhanced by a factor of 12 because of the lower sensitive of the AED for N than for S and P. If the similar chromatograms for another standard solution were shown, only

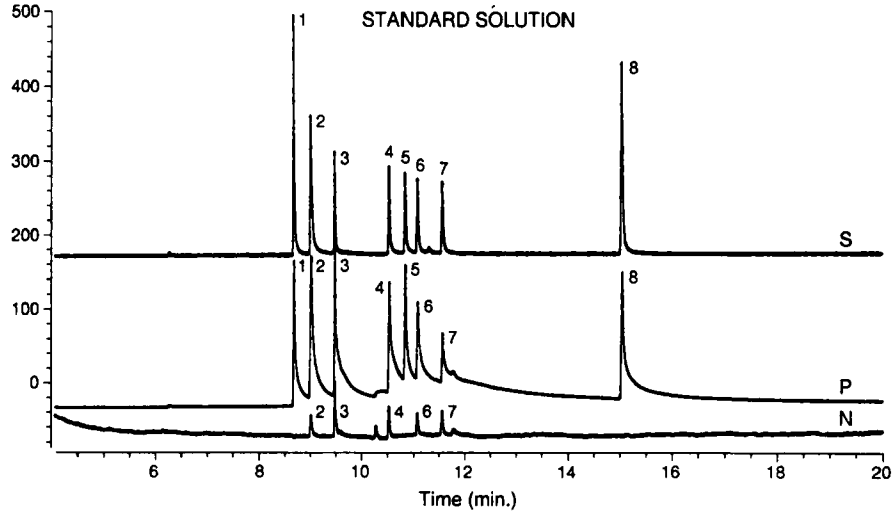

Figure 1 S, N and P element specific chromatograms of standard solution. 1. phorate, 2. dimethoate, 3. diazinon, 4. methylparathion, 5. ronnel, 6. fenitrothion, 7. parathion, and 8. ethion (1 ng/uL).

one peak would be present in the ES-P chromatogram, that corresponding to malathion, as the other compounds, butylate, diallate, triallate, metribuzin and the endosulphan do not contain the element P. The ES chromatograms for sample # 2046 are shown in Figure 2. The ES-S, P and N chromatograms are shown in Figure 2(a) and the ES-C chromatogram in Figure 2(b). The major feature the chromatograms in this figure is the large number of peaks in the ES-C chromatogram compared to the other chromatograms. All of the C-peaks related to those of the heteroatoms are minor

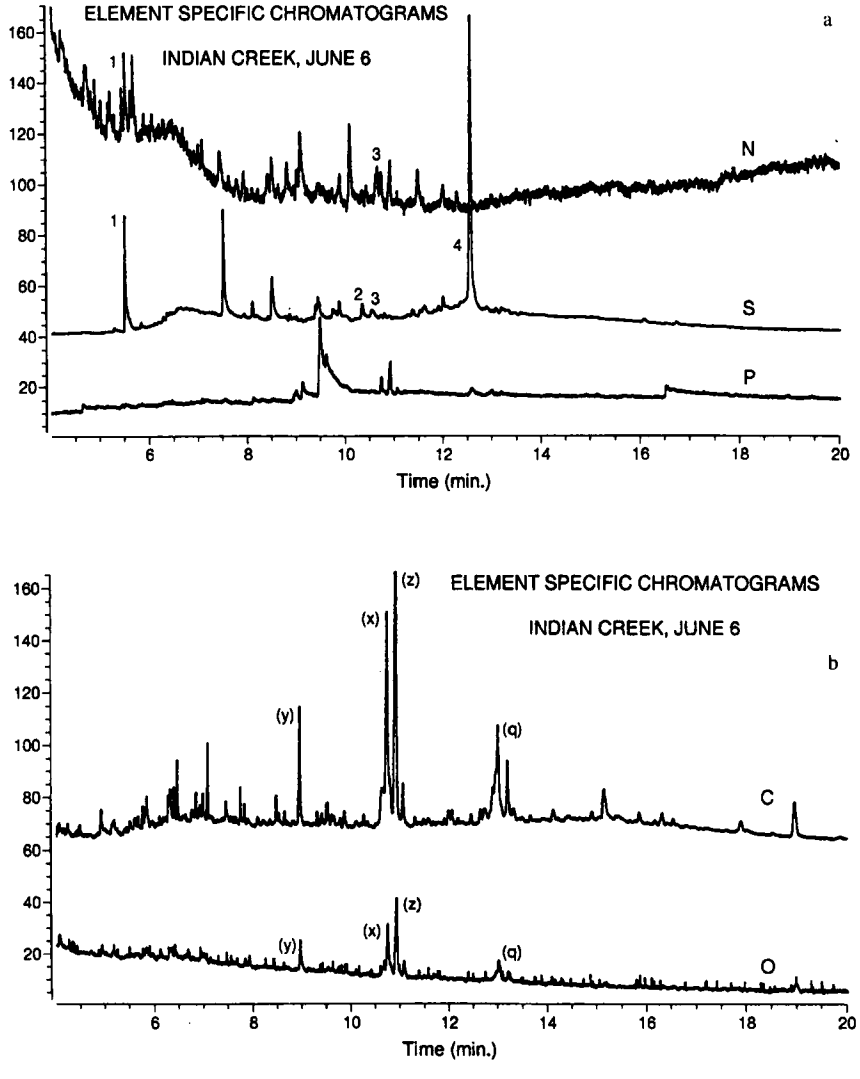

Figure 2 Element specific chromatograms of extract from Indian Creek sample. (a) S, N and P chromatograms. Compounds identified are: 1. benzothiazole; 2. metribuzin; 3. methylparathion; 4. sulphur. (S channel results attenuated to lower values to show details in P and N chromatograms). (b) C And O chromatograms. Braketed letters denote compounds containing the elements of C and O. (C channel results attenuated to show detail in the O chromatograms).

contributors in the C-chromatogram. There are over 140 peaks in this chromatogram. However there are significantly fewer peaks in the ES heteroatom chromatograms. This is true for all the samples anlayzed.

Analysis of the peaks contained in the heteroatom element specific chromatograms provides significant information related to the non target compounds in the samples. As the number of S-peaks occurring in any sample is considerably less than the number of carbon peaks, comparisons between samples is facilitated. This is accomplished by tabulating the retention times of the peaks from the element specific chromatograms. For the S-containing compounds in the precipitation run-off samples, 60 individual peaks were observed occurring in the 16 samples. Of these, 29 compounds occurred in 5 or more of the samples. Many of these occurred in 10 or more of the samples. Compounds eluting at retention times of 5.54, 8.11 and 8.53 min. occur in all samples. In the 16 samples, there were 35 different N-containing compounds, of which 23 occur in more than 2 samples. Two compounds eluting at 5.54 and 10.1 min. were observed in 15 of the 16 samples. Analysis of the ES-P chromatograms, indicated that there were 35 different P-containing compounds in the run-off samples. Of these, only 9 were detected in 2 or more samples. The peak at 9.5 min. (diazinon) was found in 7 of the samples. In addition the ES oxygen chromatograms were recorded. The O peaks eluted at the same retention times as major peaks in the ES C-chromatograms.

A similar basic analysis of the agriculture pesticide application samples was conducted. There were 27 individual S related peaks, 13 individual P related peaks and 5 nitrogen peaks. When the same criteria was used as in the runoff series of samples, there are only 7 S related peaks that were contained in 5 or more samples, 8 P related peaks that occur in more than one sample and 2 N peaks that were present in more than one sample. The areas of the peaks are generally lower than recorded for the runoff series of samples. These results were obtained from ES-chromatograms when the AED was operated at less than optimal conditions.

DISCUSSION

From the results listed in Table 1, the GC-AED technique is shown to be fully adequate to identify and quantify the S- and P- containing pesticides. The temperature program used for the AED analysis was one that was used successfully for screening a large number of fuel samples[10] and tire fire water extracts. It was not intended to differentiate between the closely eluting compounds of fonofos, diazinon, and terbufos. However, the other pesticides, if present, were detected. In addition to the determination of P-containing pesticides by NPD/ECD which was the intial intent of the study, the AED technique was used successfully to analyze for other heteroatom containing compounds which are measured by other methodologies.

As shown earlier in Figure 2(b), the ES-C chromatograms of environmental samples exhibit a complex pattern of peaks. If this sample extract was analyzed using an FID or MSD in total ion count mode and under similar chromatographic conditions, a similar peak pattern would be obtained. Interpretation of such complicated chromatograms is extremely difficult. However, the ES S-chromatograms may be easier to interpret, especially if there are a large number of such chromatograms from sample extracts pertaining to a study area. In this figure, the dominant peak in the ES-S chromatogram elutes at 5.54 min., and this peak is a major peak in the other runoff samples. The compounds eluting at 5.54 and 8.43 min. are detected in all samples. Also these two peaks have a N peak occurring at the same time in most of the samples. Those samples in

which no N-peak was detected at this time, have lower integrated area for this peak in the ES-S chromatograms. As the AED is not as sensitive to N as S, no N signal would be expected for these samples. Comparison of the molar responses for the S and N signals[10] derived from the peak areas results, (S/N) varied about 1 ± 0.2, indicating that there is a 1:1 correspondence between S and N. The areas related to the C response for this peak were tabulated with the S and N responses. The C/S and C/N values varied widely, indicating there was another compound coeluting at this time. In a previous study related to tire leachates[12], a compound eluting at this time containing both S and N was identified as benzothiazole. GC-MS analysis of one of the runoff samples confirmed that the peak eluting at 5.54 min. was benzothiazole. The concentrations of this compound in these samples were calculated from the S and then N responses, knowing the identity of the previously unknown compound. These are shown in Table 3(a). There is good agreement between the concentrations calculated independently for the S and N responses. However, the concentrations calculated from the carbon responses differ considerably from the concentrations derived from the S and N responses. When an authentic samples of this compound was later analyzed, the retention time and responses were confirmed.

It proved more difficult to determine the structure of the peak occurring at 8.54 min. Comparison of the molar S/N responses showed that there was a 1:1 correspondence between S and N, but again, the molar S/C and N/C ratios derived from peak area values, varied considerably. Despite several attempts, this peak was not identified by GC-MS. As the structure of this compounds is unknown, the concentrations cannot be calculated.

The results for the agricultural pesticide application sample extracts show that there is a ES-S peak at 5.84 min. that occurs in most of the samples. In the preliminary work on standards, this is the anticipated retention time that dibrom was expected to elute. However, dibrom (naled) contains P and no S atoms. The ES-P chromatograms of these samples contained no peaks eluting at this time. Therefore these peaks cannot be attributed to dibrom. A GC-MS examination of sample #2902, indicated that peak at 5.84 min. is benzothiazole. Accordingly, benzothiazole was found in 12 of the 17 agricultural samples. The concentrations, calculated from the S-responses, are listed in Table 3(b). There is a considerable difference in the values for benzothiazole in the two sets of samples (by factor of approximately 10). In a study conducted on a creek flowing

Table 3 Benzothiazole concentrations.

(a) Runoff samples				*(b) Agricultural samples*	
Sample #	*C ng/L*	*S ng/L*	*N ng/L*	*Sample #*	*S ng/L*
2051	3.72	1.79	1.80	3053	–
2050	1.45	1.17	2.26	4174	0.01
4176	1.80	0.59	0.76	4566	–
2046	1.74	0.57	0.84	4568	0.01
2045	–	0.56	0.73	4577	–
4171	2.53	1.57	1.77	5030	–
2042	2.50	0.67	0.80	5830	0.01
2034	–	0.77	0.54	6872	0.05
2916	4.28	1.78	3.16	6890	0.09
2915	–	1.17	1.98	6892	0.01
2912	2.17	1.24	1.62	6894	0.03
3053	0.34	0.24	–	8453	0.05
2054	1.94	0.84	0.39	8454	–
4901	1.98	1.09	1.67	8456	0.03
				8457	0.02

through an urban area[13,14], benzothiazole was detected as were other thiazoles. This creek flowed past a tire manufacturing facility. Generally the agricultural sites are not in urban areas whereas all runoff samples were collected from urban areas. However, many of the agricultural sampling sites were located downstream from major highways which pass through the study areas.

Other generalizations can be made from the ES chromatograms. First is that there were more S peaks observed in the chromatograms from the urban runoff samples than from the agricultural samples. This is also reflected in the number of peaks of the ES-N and ES-P peaks in the chromatograms of the two sets of samples. Area values of the S and P peaks for standards were similar during both sets of analysis.

To this point only the general characteristics of two sets of surface water samples have been considered. More information is available in the chromatograms obtained from these samples. Both the urban samples and agricultural spraying samples have been lumped as two cases. When the actual sites relative to other sites of the same collection type, e.g. urban runoff, are compared, other trends may be apparent. Figure 3 illustrates the ES-S chromatograms for samples from 6 locations, collected in late May. To illustrate some of the detail contained in the co-plotted chromatograms, that from Spencer Creek was multiplied by 0.5. Certain similarities are apparent. All have peaks at 5.54 and 8.5 min. and all contain certain target compounds. The differences are more abundant. Only two chromatograms exhibit the major S_8 peak while the other four have minor peaks for this element. The total area contained under the S peaks vary.

Figure 4 shows the ES-S chromatograms for the extracts of Indian Creek samples collected during the first two days of a three day precipitation event. The bottom chromatogram was of a sample taken during the first few hours of the event. The upper chromatogram was of an extract collected the next day when there was a higher flow, greater water turbidity and more debris was observed in the creek. This chromatogram exhibits a strong S_8 peak at 12.4 min., which is only a minor peak in the bottom chromatogram as well as a peak at 7.53 min. which does not occur in the lower chromatogram. Many of the smaller peaks occur in both chromatograms. The benzothiazole peak (5.54 min.) is slightly larger in the bottom chromatogram as is the peak at 8.38 min. If the benzothiazole peak is related to tire usage, the concentration of this peak would be expected to be very much smaller in the top chromatogram than the bottom. This results from any build up of this chemical near the road would be expected to be highest shortly after the start of the precipitation event when it is washed into the creek. The similar peak height observed in the sample collected 24 hours later may result from material originally bound to suspended material. However the benzothiazole peak was found in non-event samples, as seen in the next figure. Figure 5 shows the ES-S chromatograms for Indian Creek sample extracts which were collected over 1.5 months. The sample collected on June 24 was collected when there was no precipitation event several days prior to sampling which was defined as base flow. The June 19 sample was collected after an event of short duration, circa 30 min., with 2 mm of precipitation. The June extracts both contained a compound which eluted at 5.8 min. and three compounds which eluted between the 8 and 9 min. interval. One of these peaks, diazinon, was found in the extract of all 4 samples. The other two chromatograms were from extracts of samples collected during precipitation events. All samples contain elemental sulfur. The two chromatograms of extracts of samples collected when there was little or no precipitation (June 19 and June 24) have the smallest S_8 peaks, whereas the other two chromatograms, from samples collected when there were greater than 5 cm of precipitation, exhibit significantly larger S_8 peaks. In Figure 4, the peak corresponding to S_8 is greater in the extract of the sample collected after 24 hours of precipitation than that from the one collected shortly after the event began.

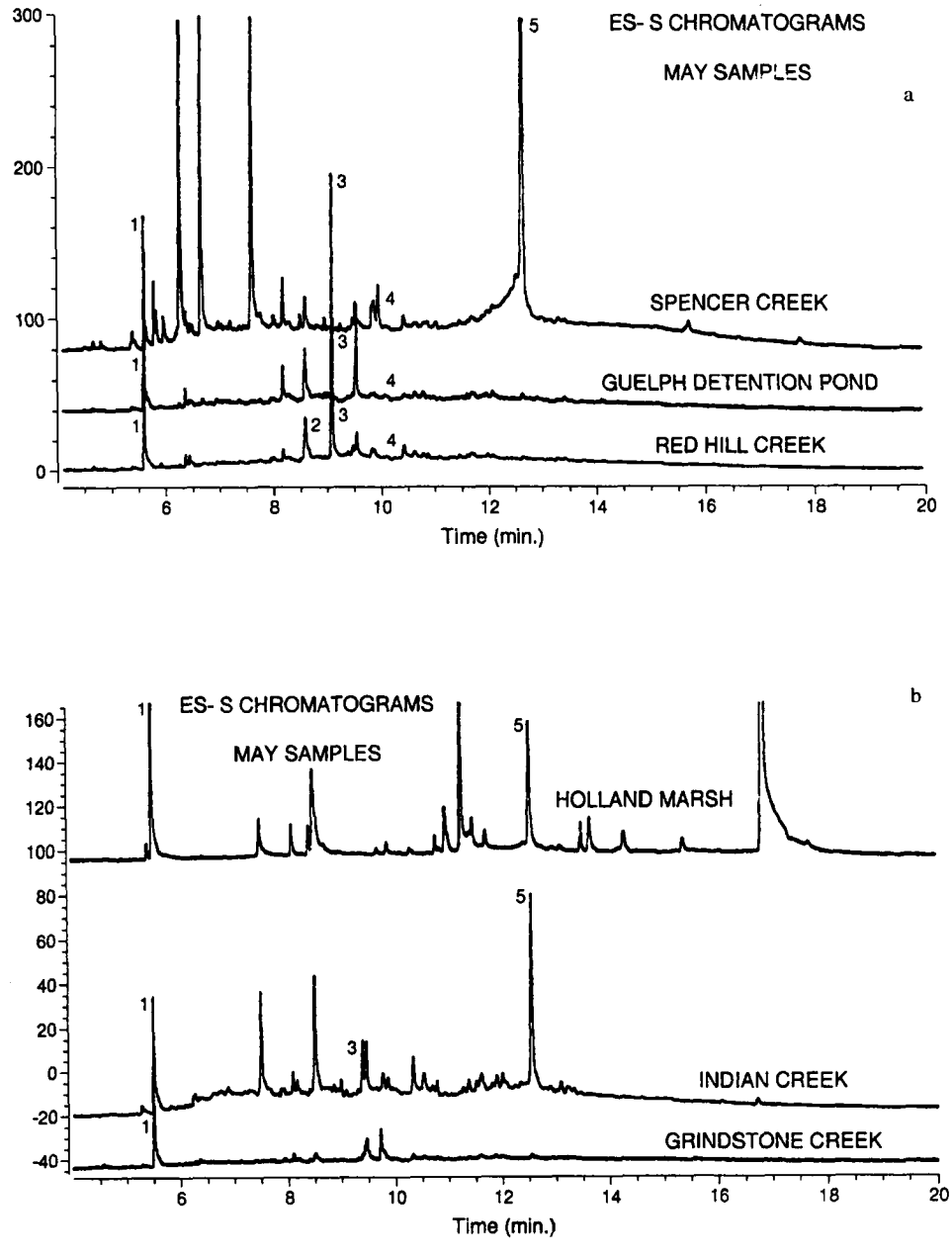

Figure 3 S-element specific chromatograms of extracts collected in May from (a) Holland Marsh, Indian Creek, and Grinstone Creek, and (b) Spencer Creek, Guelph Detention Pond, and Red Hill Creek. Peaks identified are: 1. benzothiazole; 2. diallate; 3. diazinon; 4. metribuzin; 5. sulfur.

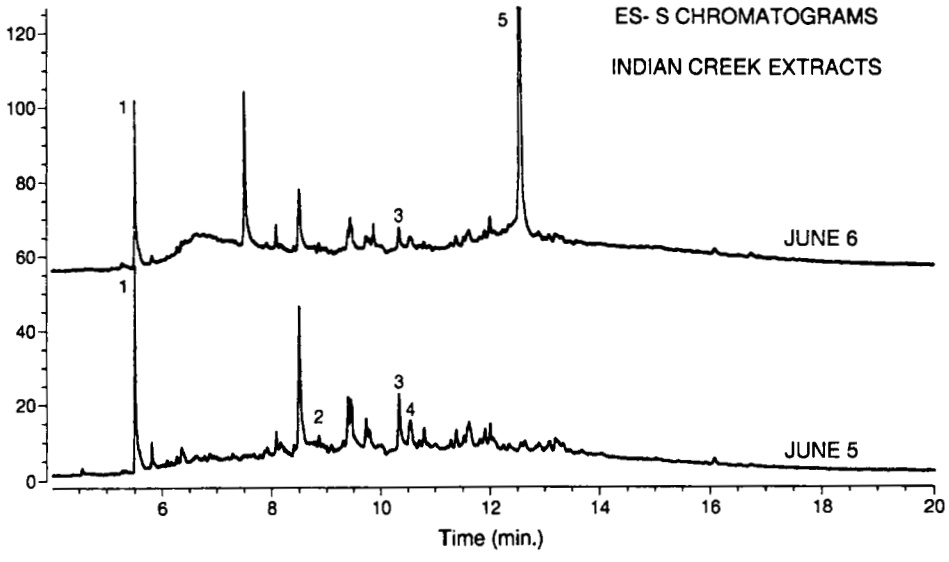

Figure 4 S-element specific chromatograms of Indian Creek extracts collected on different days during and extended precipitation event. Compounds identified are: 1. benzothiazole; 2. diallate; 3. metribuzin; 4. methylparathion; 5. sulphur.

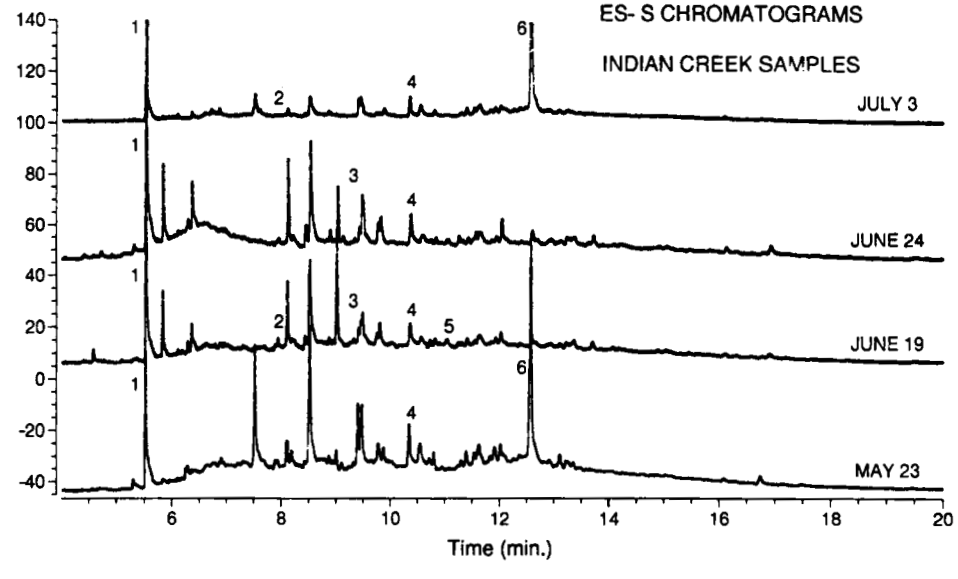

Figure 5 S-element specific chromatograms of Indian Creek extracts collected over sampling season. Compounds identified are: 1. benzothiazole; 2. dimethoate; 3. diazinon; 4. metribuzin; 5. malathion; 6. sulfur.

There are differences between the results obtained from the agricultural samples and those obtained from the urban runoff, in the two sets of results. Fewer S, N and P peaks were observed in the respective chromatograms for the agricultural samples than the urban samples. This in part was caused by the decreased sensitivity of the AED when analyzing the agricultural samples.

For the present study, The AED analysis was conducted after the samples had been archived. If sufficient sample extract was available, additional column chromatography would have been undertaken to facilitate more extensive GC-MS analysis for those compounds which occur in many of the samples. This preliminary study will assist in the design of sampling strategies for future studies. In addition, once these strategies are formulated, quality assurance procedures can be incorporated into the collection and analysis procedures.

CONCLUSIONS

The GC-AED technique is shown to provide a facile method to obtain a better understanding of the organics in surface water. In most studies, determination of the presence and concentration of target compounds is the major objective. By using the detection capabilities of the AE detector, valuable information is available to not only the analyst and the environmentalist but to those charged with water management. This is achieved by collating the results obtained from the heteroatom ES chromatograms. It is easier to identify trends using a small number of peaks as generated from the ES heteroatom chromatograms, than by attempting to interpret chromatograms which result from some property inheret of the majority of organic compounds in the extracted sample as in the case of flame ionization, mass spectral or electron capture detector.

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References

1. L. M. Pope and H. E. Bevans, U. S. Geological Survey Water-Supply Paper 2283.
2. R. N. Oltmann and M. V. Shulter, U. S. Geological Survey water-supply paper; 2335.
3. D. B. Baker, *Ag. Ecosys. Environ.*, **46,** 197–215 (1993).
4. H. J. Nesbitt and J. R. Watson, *Water Res.*, **14,** 1683–1688 (1980).
5. G. D. Foster, P. M. Gates, W. T. Foreman, S. W. McKenzie and F. A. Rinella, *Environ. Sci. Technol.*, **27,** 1911–1917 (1993).
6. J. C. Merriman, D. H. J. Anthony, J. A. Kraft and R. J. Wilkinson, *Chemosphere*, **23,** 1605–1615 (1991).
7. Analytical Protocol for Monitoring Ambient Water Quality at the Niagara-on-the-Lake and Fort Erie Stations, Environment Canada, National Water Quality Laboratory, Burlington, Ontario, 1987.
8. B. D. Quimby and J. J. Sullivan, *Anal. Chem.*, **62,** 127–34 (1990).
9. J. J. Sullivan and B. D. Quimby, *Anal. Chem.*, **62,** 1034–43 (1990).
10. B. F. Scott and E. Nagy, NWRI Contribution No. 93–63.
11. B. F. Scott and A. Cassista, *Proc. Environ. Contaminants*, Barcelona, Oct. 1–4, (1990), p. 91.
12. J. H. Carey, M. E. Fox, B. G. Brownlee, J. L. Metcalfe, P. D. Mason and W. H. Yerex, N.W.R.I. Scientific Series #135, 1983, Environment Canada, Burlington, Ontario.
13. J. L. Smith, M. E. Fox and J. H. Carey, *Environ. Monitoring*, **11,** 147–69 (1988).
14. B. G. Brownlee, J. H. Carey, G. A. MacInnis and I. T. Pellizzari, *Environ. Toxicol. Chem.*, **11,** 1153–68 (1992).