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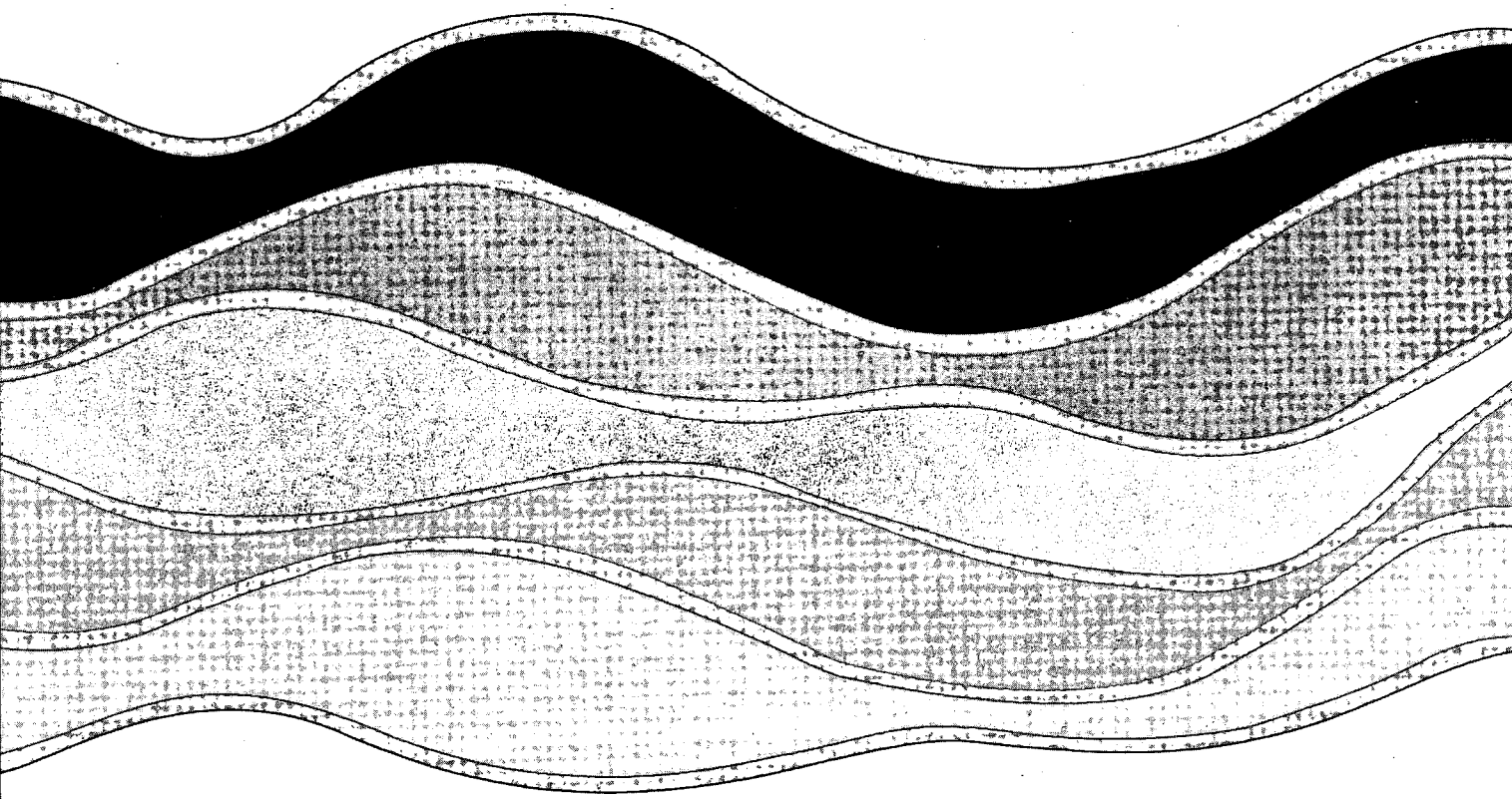

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NWRI Contribution No. 94-51

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MANAGEMENT PERSPECTIVE

This report describes a study which investigated the analysis of phosphorus containing pesticides in urban and agricultural drainage waters by GC/atomic emission detection (AED). The detection of target pesticides and their concentrations obtained from the GC/AED method was shown to be comparable with those from the standard method of analysis. Moreover, as the AED is essentially element specific, it permitted simultaneous detection of other pesticides containing S, N, and/or P. The analysis of these compounds would normally require additional methods. The simplified heteroatom chromatograms also facilitated the identification of an unsought compound, benzothiazole which was present in 27 of the 34 samples. The GC/AED technique possesses excellent potential for the comprehensive analyses of organics in water samples.

SOMMAIRE À L'INTENTION DE LA DIRECTION

Le présent rapport décrit une étude sur l'analyse des pesticides renfermant du phosphore dans des eaux de drainage urbaines et agricoles par CG/détection par émission atomique (DEA). La détection des pesticides cibles et leur concentration obtenue par CG/DEA se compare à ce qu'on obtient par la méthode d'analyse standard. En outre, comme la détection par émission atomique est essentiellement spécifique d'un élément, on peut détecter simultanément d'autres pesticides renfermant du S, du N, et/ou du P. Il faudrait normalement d'autres méthode pour analyser ces composés. Les chromatogrammes simplifiés d'hétéroatomes ont également facilité l'identification d'un composé non recherché, le benzothiazole, qui était présent dans 27 des 34 échantillons. La technique de CG/DEA comporte d'excellentes possibilitiés pour l'analyse détaillée des composés organiques dans les échantillons d'eau.

ABSTRACT

In two separate pesticide monitoring studies, surface water samples were collected from different locations in southern Ontario. Following clean up, the extracts were analyzed for selected P-containing pesticides using capillary column GC equipped with N/P and ECD detectors. These extracts were then 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. In addition to the P-containing chemicals, which were mainly the target compounds, 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.

RÉSUMÉ

Dans deux études distinctes dans le cadre de la surveillance des pesticides, on a prélevé des échantillons d'eau de surface à différents endroits dans le sud de l'Ontario. Après purification, les extraits ont fait l'objet d'une analyse de certains pesticides renfermant du P au moyen de la CG sur colonne capillaire munie de détecteurs de N/P (DNP) et de capture d'électrons (DCE). Ces extraits ont ensuite été analysés par CG/DEA pour détecter les composés renfermant du C, du S, du N, du P et de 1'0. Tous les composés cibles identifiés par CG/DNP/DCE ont été détectés à l'aide de la technique de CG/DEA. Les deux méthodes d'analyse ont donné des résultats qui ont permis de calculer des concentrations comparables pour les composés cibles. En plus des composés renfermant du P qui étaient les principaux composés cibles, on a identifié d'autres composés renfermant du S et du N dans les échantillons. Les pics ont été identifiés au moyen de leur temps de rétention et de leur réponse. L'un de ces composés, le benzothiazole, a été retrouvé dans 27 des 34 échantillons.

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 organic chemicals in surface waters flowing through agricultural areas after pesticide application. The second was the 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 expended 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 (e.g. 5) as well as in monitoring (e.g.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 (e.g.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 too 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 hetero-element chromatograms.

With atomic emission detection, analysis of the 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 C and H. With fewer peaks to consider, correlations 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 detail 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 (10). The samples were analyzed using the GC/AED technique. Once the target compounds had been determined, the remaining peaks in the element specific heteroatom chromatograms would be evaluated. The atoms of interest were C, S, N, P, and O.

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, were root crops are prevalent. The other area was in the Niagara Peninsula were 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 subdivisions. Appropriate control samples were also taken prior to events. The other area was the Hamilton Harbour watershed. In this area, streams flowing into harbor 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 in glass bottles then returned to the laboratory for clean up, extraction (10) and analysis. The neutral extracts of the samples were analyzed for the organophosphorus insecticides, the target compounds, by dual detector GC/NPD/ECD with confirmation by GC/MSD.

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 and the photodiode array covered the range of 250 nm, 3 different injections were required for each sample with each one 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 mL were made in the splitless mode. A SE52-XL column, 30m X 0.25mm id, with a film thickness of .25u was supplied by Hiresco (Mississauga, Ont.).

The primary standards were phorate ($C_7H_{17}O_2SP$), dimethoate ($C_5H_{12}O_3S_2NP$), diazinon ($C_{12}H_{21}O_3SN_2P$), ronnel ($C_8H_8O_3SPCl_3$), phosphamidon ($C_{10}H_{19}O_5PNCl$), methylparathion ($C_8H_{10}O_5SNP$), parathion ($C_{10}H_{14}O_5SNP$), cruformate ($C_{12}H_{19}O_2PNCl$), ethion ($C_9H_{22}O_4S_4P_2$), phosmet ($C_{11}H_{12}O_4S_2NP$), malathion ($C_{10}H_{19}O_6S_2P$), azinphosethyl ($C_{12}H_{16}O_3S_2N_3P$), azinphosmethyl ($C_{10}H_{12}O_3S_2N_3P$), butylate ($C_{11}H_{19}OSN$), diallate ($C_{10}H_{17}OSNCl_2$), triallate ($C_{10}H_{16}OSNCl_3$), metribuzin ($C_8H_{14}OSN$), a-endosulphan and b-endosulphan ($C_9H_6O_3SCl_6$). These were divided into three solutions with each compound having a concentration of 1ng/mL. Additional standard solutions containing fonofos, chlopyrifos and dibrom (naled) were also used.

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 IA. 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. The response of the AED signal for S was used to determine similar concentrations. 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 $\pm$ 0.05 min. with this temperature program. Therefore the initial entries in Table I(a) have no AED result to compare to the NPD/ECD results, although small peaks were observed in the element specific S 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 fitting 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 precipitation run-off samples were then analyzed as were three additional pesticide application samples. These results are contained in Table I(b) as are the NPD/ECD method results. There is a good agreement between the NPD/ECD and the AED results, first with respect to the identity of compounds in the samples and second with respect to their concentrations. The agreement between the concentrations determined by the two techniques, listed in Table I, is within a factor of 5, usually within a factor of 2. Only in two instances of the results presented in this table does the AED fail to determine a compound identified by the other method, which was diazinon.

Table II 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 most frequently identified known compound in the runoff samples was metribuzin, as identified from the ES-S chromatograms. 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. Certain 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, the response is not linear (12). 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 II were determined from the S response.

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 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 Fig 2. The ES - S, P and N chromatograms are shown in Fig. 2A and the ES-C chromatogram in Fig. 2B. 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 contributors in the C-chromatogram. There are over 140 peaks in this chromatogram. However there are significantly fewer peaks in the ES-S chromatogram. This is true for all the samples analyzed. There were also peaks not related to the target compounds in the ES-P and -N chromatograms. In the 16 runoff samples analyzed, there were 60 different S peaks, 33 different N peaks and 35 P different peaks detected as well as 22 O peaks.

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, the occurrence of the S-peaks in the samples can be tabulated. This is shown in Table III(a) for the run off samples where only those peaks which occur in 5 or more samples as denoted by their retention times are included. Their presence is indicated by symbols which are related to the concentration (integrated peakarea). In Table III, the symbols s, m, l and L were chosen to denote area counts of 0 to 100 = s, 100 to 1000 = m, 1000 to 10000 =l and over 10000 = L. The other heteroatoms peaks, such as N and P are also tabulated using the same designations in Table III. This permits facile comparison of retention times between the heteroatoms. Examination of Table III(a) shows that some S-peaks occur in only a few samples while other peaks are observed in all samples. The number of peaks for a particular sample is also given in the table. There are 29 different retention time headings in Table III(a), and 31 other retention times not shown as they occur in less than 5 samples. Compounds eluting at retention times of 5.54, 8.11 and 8.53 min. occur in all samples. Many of the 29 peaks noted in the table occur in more than 10 of the samples.

Table III(b) contains similar data related to the nitrogen containing compounds. Only those peaks which occur in 2 or more of the of the samples are listed. There are 23 entries for the 16 samples and 12 peaks occur in single samples. Of the 23 entries, 4 of the compounds occur in two samples. For the N- and S-containing compounds, the majority of the compounds occur in over 50% of the samples. The legend of s, m and l used in Table III(b) is the same as used for Table III(a). The most notable difference is the lack of many peaks designated as l. This is related to the sensitivity of the AED to N. No N-containing compound is found in all of the samples, but two compounds are found in 15 of the samples, namely those two eluting at 5.55 and 10.1 min.

Table III(c) lists the retention times and relative responses (s, m, or l) for the P-containing peaks that occur in 2 or more of the samples. Only 9 retention times are

included in this section of the table. Of the 35 original peaks, 26 occur in single individual samples. Phosphorus is as sensitive as S by AED detection, but only one of the peaks in this table is designated as l. Indeed, only one half of the entries occur in more than two of the samples, with the entry at 9.50 min. being found in 7 of the samples. In addition the ES oxygen chromatograms were recorded and these results are given in Table III(d). For this element, all peaks are listed in the table. 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 are listed in Table IV. Initially 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 as shown in Table IV(a), 8 P related peaks that occur in more than one sample and 2 nitrogen 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 I, the GC/AED technique is shown to be fully adequate to identify and quantify the S- and P- containing pesticides. The program temperature used for the AED analysis was one that was used successfully for screening a large number of fuel samples and tire fire water extracts (11). 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 initial intent of the study, the AED technique was used to successfully analyzed for other heteroatom containing compounds which are measured by other methodologies (12, 13).

As shown earlier in Fig.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. From Table III(a), the compounds occurs at 5.54 and 8.43 min. are detected in all samples. Also these two peaks have a N peak occuring at the same time in most of the samples. Those samples in which no N-peak was detected, have lower S signals as denoted by the "m" in Table III(a) for sample #3053. This sample had the lowest area measure for this peak. As the AED is not as sensitive to N as S, no N signal would be expected for this sample. Comparison of the molar responses for the S and N signals (14) derived from the peak areas results, (C/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. This coeluting compound contains carbon but no S and N. In a previous study related to tire leachates (14), 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 V(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 sample of this compound was later analyzed, the retention time and responses were confirmed.

It proved more difficult to determine the structure of the peak occuring 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. This peak was not identified by GC/MS. As the structure of this compound is unknown, the concentrations cannot be calculated.

The results for the agricultural pesticide application sample extracts given in Table IV shows 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 occuring at this time. Therefore these peaks cannot be attributed to dibrom. The majority of the agriculture pesticide application samples were analyzed before the runoff samples, which were analyzed using a slightly increased carrier gas flow rate. Examination of the retention times of the standards analyzed under both flow rate conditions indicated that the peak observed in the runoff samples indicate that peaks at 5.84 min. in these samples would occur at 5.51 min. under the conditions that the runoff samples were analyzed. This is close to the benzothiazole retention time measured in the runoff samples. The three agricultural pesticide application samples analyzed with the runoff samples were from the same area as those analyzed previously, and two of the three samples had a ES -S peak at 5.54 min. as well as a ES-N peak occuring at the same time. Unlike the responses in the runoff sample extracts, no peak was observed in the ES-N chromatograms at 5.84min. in the agricultural pesticide application sample extracts. However an examination of the ES-S response shows that the areas of the ES-S peaks at 5.84 min. are considerably smaller, as denoted by the "m" and "s" designations in Table IV(a) as compared to the "l" and "m" values in Table III(a) for the peak at 5.54 min. As the ES-N sensitivity is lower than the ES-S sensitivity, the compound at 5.84 min. is not present in sufficient concentration to provide a signal on the N-channel. A GC/MS examination of sample #2902, indicated that the peak at 5.84 min. is benzothiazole. Accordingly, benzothiazole was found in 12 of the 17 agricultural samples listed in Table IV. The concentrations, calculated from the S-responses, are

listed in Table V as well. 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 through an urban area, (13,14), benzothiazole was detected as were other thiazoles. This creek was the water course flowing 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 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 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. run off, are compared, other trends may be apparent. Fig. 3 illustrates the ES-S chromatograms for samples from 6 locations, collected in May. To illustrate some of the detail contained in the co-plotted chromatograms, that from Spenser 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.

Fig. 4 shows the ES-S chromatograms for the extracts of Indian Creek samples collected during an event that lasted 3 days. The top chromatogram was of a sample taken during the first few hours of the event. This chromatogram exhibits a strong S_8 peak at 12.4 min., which is only a minor peak in the bottom chromatogram. The benzothiazole

peak (5.54 min.) is slightly larger in the bottom chromatogram as is the peak at 8.38 min. These chromatograms illustrate the extent of flushing of the system, which is important to the interpretation of the chromatograms. Fig. 5 shows the ES-S chromatograms for Indian Creek sample extracts which were collected over 2.5 months. The sample collected on June 24 represents base flow and was not influenced by a storm event. 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 compounds which eluted at 5.8 min. and three compounds which eluted between the 8 and 9 min. interval. One of these peaks was found in the extract of all 4 samples. The other two chromatograms represented normal events. All samples contain elemental sulfur. Samples collected during precipitation events would transport compounds into the water ways or creeks, but the larger amount of receiving water would cause some dilution. Also the time of collection is another factor, viz. day or month, and this connected to natural or anthropogenic events such as precipitation or pesticide application may provide other insights.

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 inherent 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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CAPTIONS FOR FIGURES

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).

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).

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. metibuzin; 4. methyl-parathion; 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.

TABLE I

(a) COMPOUNDS IDENTIFIED IN AGRICULTURAL SAMPLES BY GC/NPD/ECD AND GC/AED (in ng/L)

Sample #	Location	Compound	NPD/ECD	AED (S-channel)
2902	HM	fonofos	74	
		malathion	38	
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

(b) COMPOUNDS IDENTIFIED IN RUNOFF SAMPLES BY CG/NPD/ECD AND GC/AED (in ng/L)

Sample #	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	
2916	HH-IC	dimethoate	159	160
		diazinon	354	400
4176	HH-IC			
2046,2042, 2034	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

TABLE II

OTHER COMPOUNDS IDENTIFIED IN SAMPLES USING GC/AED TECHNIQUE (ng/L)

(a) Runoff samples

Sample No.	Compound	Concentration
2050	diallate	150
	metribuzin	125
2051	metribuzin	450
2054	diallate	20
	metribuzin	p
2912	metribuzin	445
	malathion	370
2915	ronnel	p
3397	butyate	85
	metribuzin	185
	malathion	32
4901	diallate	135
	metribuzin	465
4902	metribuzin	465
3053	diazinon	665
	parathion	100

b) Agricultural Samples

Sample #	Compound	Concentration
2902	parathion	20
	ethion	50
5030	parathion	160
	ethion	88
5820	diazinon	70
	ethion	35
6272	diallate	811
	parathion	350
	ethion	210
6890	dimethoate	150
6894	dimethoate	52
8453	dimethoate	100
8456	dimethoate	53
4567	α-endosulphan	80
	ß-endosulphan	51

TABLE III(a)

Compilation of S Peaks

Rt	#peaks	5.54	6.3	6.38	6.59	7.54	8.11	8.2	8.43	8.53	9.42	9.46
Sample#		Guelph Retention Ponds										
2050	15	l	m				m			l	m	
4901	25	l		s			m	m		m		
8457	(6)	(s)										
		Indian Creek										
2034	18	l	m			l	l	m		l	m	
2042	25	l	s	m	s		m	m	s	m	m	m
2046	29	m	s	s	m	l	m			m	m	m
2912	27	l	s	m	s		m	m	m	l	m	
2916	25	l		m	s		m	m	m	l		
4176	21	m		s		m	s			m		m
		Grindstone Creek										
2045	9	m		s			s			m	s	
2915	30	l	m	s	m	m	m	m	s	m	m	
3397	26	l				l	m			m		m
		Red Hill Creek										
2054	22	l	m	m		s	m	s		l	m	
		Spencer Creek										
2051	32	l	m	m	l	L	m	m	m	l		
		Holland Marsh										
3053	13	l										
4171	28	l				m	m		m	l		
4173	1											

Rt	9.74	9.8	9.89	10.56	10.79	10.82	11.53	11.63	11.92	12.02	12.58	12.91
Sample#		Guelph Retention Ponds										
2050	m	m		m				m			m	
4901	m	m		m		m	s			s	m	s
8457												
		Indian Creek										
2034			m	m	m		m	m			l	
2042	m	m	m	m	s	s						
2046	s	s	m	m	s	s	s	m	m	m	l	
2912	m	m		m		m	s	m	s	s	s	
2916		m		m		s	m	m	s	m	m	s
4176			s	m		s	s	m	s	s	l	
		Grindstone Creek										
2045	m	m									s	
2915	l			m		m	m	m	m	m	m	m
3397	l	l		m			m	m	m	m	L	m
		Red Hill Creek										
2054	m	m		m		m	s	m				

TABLE III(a) (Cont.)

Rt	9.74	9.8	9.89	10.56	10.79	10.82	11.53	11.63	11.92	12.02	12.58	12.91
		Spencer Creek										
2051		l	l	m	m		m	l	l	l	L	
		Holland Marsh										
5030											s	
4171			m		m						l	
4173												

TABLE III(b)

Compilation of N Peaks

Rt	4.74	4.93	5.23	5.55	5.59	5.72	6.02	6.08	6.46	7.1	7.47	7.79
Sample#		Guelph Retention Ponds										
2050	m	s		m		m	s	s	s			
4901	m	s		m		s						
8457												
		Indian Creek										
2034	s	s		s			s	s		s		
2042	m	s	s	s		s		s	s			
2046	s	s	s	s					s		ss	
2912	s	s	s	m		m	s				s	
2916	m	m	s	m		m	s					
4176				s		s						
		Grindstone Creek										
2045	s		s	s								s
2915	m	m	s	m		m						
3397	m	s		s							s	
		Red Hill Creek										
2054				m		s	s					
7933												
		Spenser Creek										
2051	s	s	s	m	m	m	s	l	s	m	m	m
		Holland Marsh										
3053	s											
4171												
4173												

Rt	8.54	9.05	9.12	9.5	9.89	10.1	10.69	11.1	11.4	11.5	17.3
Sample#		Guelph Retention Ponds									
2050	m	s	m	m		m				m	
4901			s	m		s					
8457											
		Indian Creek									
2034	m	s	m	s		m					
2042	s	s		s		m	s				
2046	s		s		s	s				s	
2912	s	m	m			m	m	s			
2916	s	l		s		m	m	m			
4176		s				s					
		Grindstone Creek									
2045		s		s		s				s	
2915		m	m			m					
3397		l		s		s	m				

TABLE III(b) (Cont.)

Rt	8.54	9.05	9.12	9.5	9.89	10.1	10.69	11.1	11.4	11.5	17.3
		Red Hill Creek									
2054	s	m		s		m	m	m	s		
7933											
		Spencer Creek									
2051	s	m	m	m	m	m		m		m	s
		Holland Marsh									
3053				s			s				
4171											
4173											

TABLE III(c)

Compilation of P Peaks

Rt	5.54	7.53	8.16	9.02	9.14	9.5	10.9	11.1	11.2	12.6	17.9
Sample #		Guelph Retention Ponds									
2050											
4901						m					
8457											
		Indian Creek									
2034											
2042				s	m	m					
2046					s	m	m				
2912	s		s	m	m	m		s			
2916								s	s		
4176			s			s				s	
		Grindstone Creek									
2045				s		m					
2915											
3397		s		s			s		s	s	s
		Red Hill Creek									
2054											
		Spencer Creek									
2051											
		Holland Marsh									
3053	s					l					
4171	s										s
4173											

TABLE III(d)

Compilation of O Peaks

Rt(min)	3.67	4.09	4.1	4.74	4.98	5.13	5.15	5.86	6.12	6.96	8.2	8.99	10.8
Sample#		Guelph Retention Ponds											
2050		m			m								m
4901													
8457													
		Indian Creek											
2034					m		m	m	m				l
2042					m		m		m	m		m	m
2046								m	m	m		m	m
2912			m		m			m					m
2916	l			m									
4176													
		Grindstone Creek											
2045			m		m								m
2915	l	m			m								m
3397												m	l
		Red Hill Creek											
2054												m	m
7933													
		Spenser Creek											
2051													
		Holland Marsh											
3053													
4171													
4173													

Rt	10.9	11.1	13.2	13.5	13.8	16.1
Sample#		Guelph Retention Ponds				
2050	l	m				
4901						
8457						
		Indian Creek				
2034	l		m			
2042						
2046	m		m			
2912	m	m				
2916	m					
4176						
		Grindstone Creek				
2045	m		m			
2915	m	m				
3397	m					
		Red Hill Creek				

2054&7933

TABLE III(d) (cont.)

	Spencer Creek			
2051				
	Holland Marsh			
3053		m	m	m
4171				
4173				

TABLE IV

(a)Compilation of S Peaks

Rt(min)	5.84	7.93	8.33	9.72	11.5	13.26
Sample #						
4566						
4568	s					
4567						
4173	s	l		m		L
4174	s	s		l		L
5030		l		l		
5820	s	l	m	m		L
6872	s	m				
6890	m	s	m	m	m	L
2902	s				s	
6892	s				s	
8453	s					
8454			s			
6894	s				s	
8456	s		s		s	
8457	s		s			
7933						

(b) Compilation of N Peaks

Rt(min)	11.21	11.29
Sample #		
4566		
4568		
4567		
4173		
4174		
5030	m	
5820		
6872	m	
6890		m
2902		

TABLE IV (Cont.)

(b) Compilation of N Peaks

Rt(min)	11.21	11.29
Sample #		
6892		
8453		m
8454		
6894		
8456		
8457		
7933		

(c) Compilation of P Peaks

Rt(min)	7.93	9.72	12.11	13.22
Sample #				
4566				
4568				
4567				
4173	m			
4174	s	s		
5030	s			s
5820	s		m	
6872	s	s		m
6890	s		l	m
2902				
6892				
8453				
8454				
6894				
8456				
8457				
7933				

TABLE V

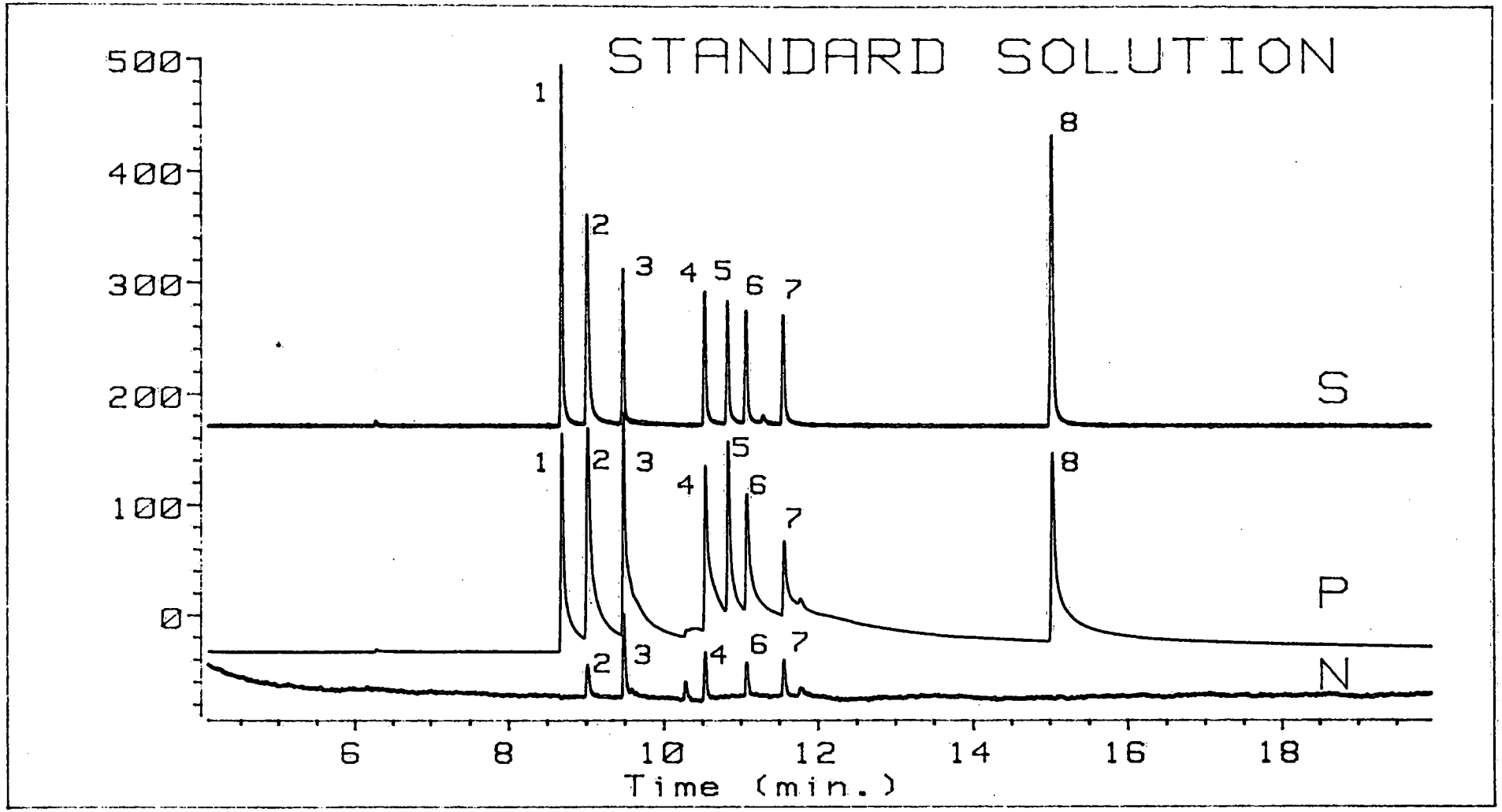
Benzothiazole concentrations

(a) Runoff Samples

	ng/L C	ng/L S	ng/L N
4902	1.67	1.18	1.52
2051	3.72	1.79	1.8
3397	0	0.66	0.73
2050	1.45	1.17	2.26
4176	1.8	0.59	0.76
2046	1.74	0.57	0.84
2045		0.56	0.73
4171	2.53	1.57	1.77
2042	2.5	0.67	0.8
2034		0.77	0.54
2916	4.28	1.78	3.16
2915		1.17	1.98
2912	2.17	1.24	1.62
3053	0.34	0.24	
2054	1.94	0.84	0.39
4901	1.98	1.09	1.67

(b) Agricultural Samples

Sample #	ng/L S
2902	0.009
3053	
4173	0.015
4174	0.013
4566	
4568	0.008
4577	
5030	
5820	0.014
6872	0.046
6890	0.09
6892	0.014
6894	0.034
8453	0.049
8454	
8456	0.026
8457	0.019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300
200
100
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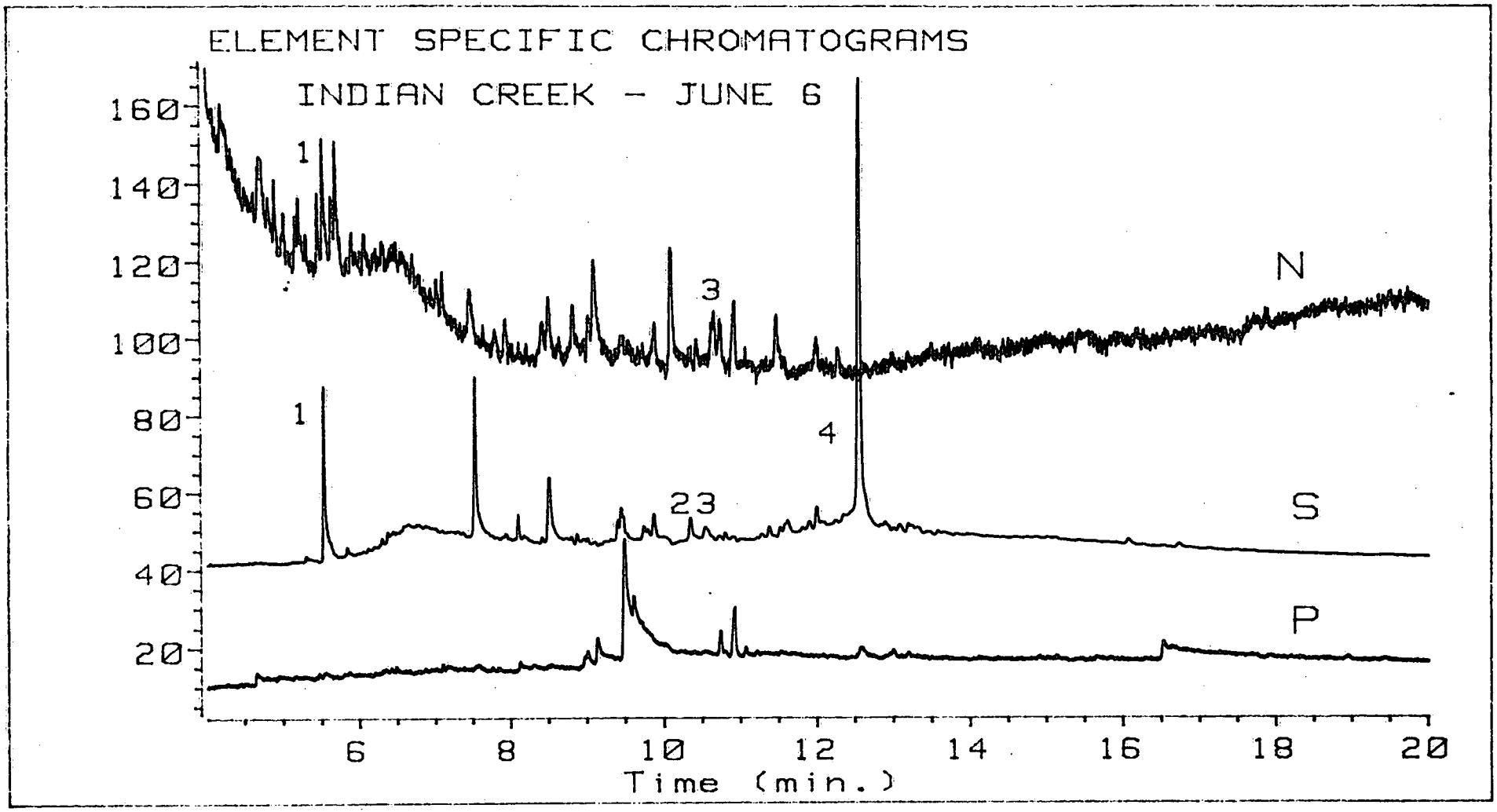
1
2
3
4
5
6
7
8
S
P
N
6
8
10
12
14
16
18
Time (min.)

FIGURE 1.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INDIAN CREEK - JUNE 6
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120
100
80
60
40
20
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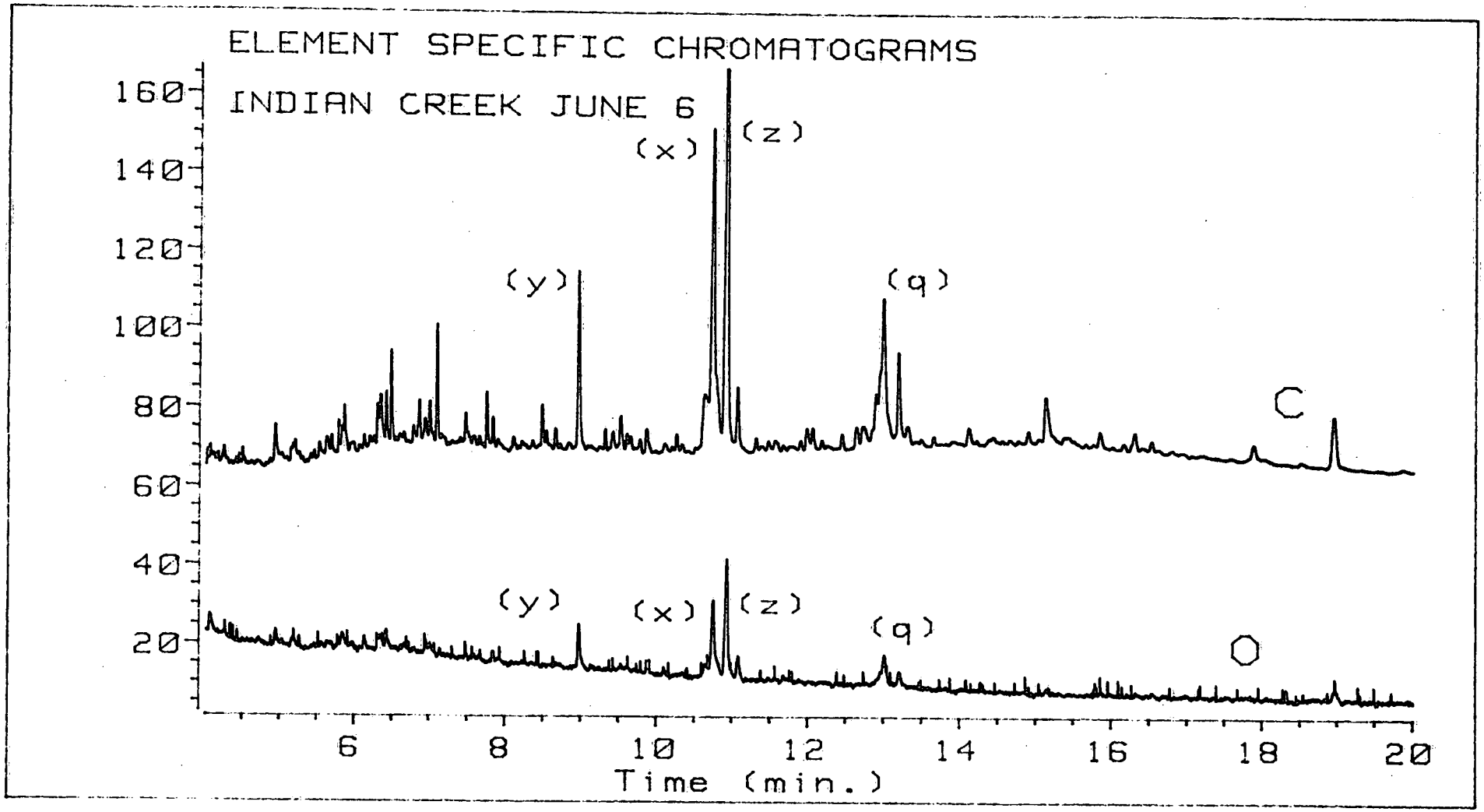
4
23
S
P
6
8
10
12
14
16
18
20
Time (min.)

FIGURE 2(a).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INDIAN CREEK JUNE 6
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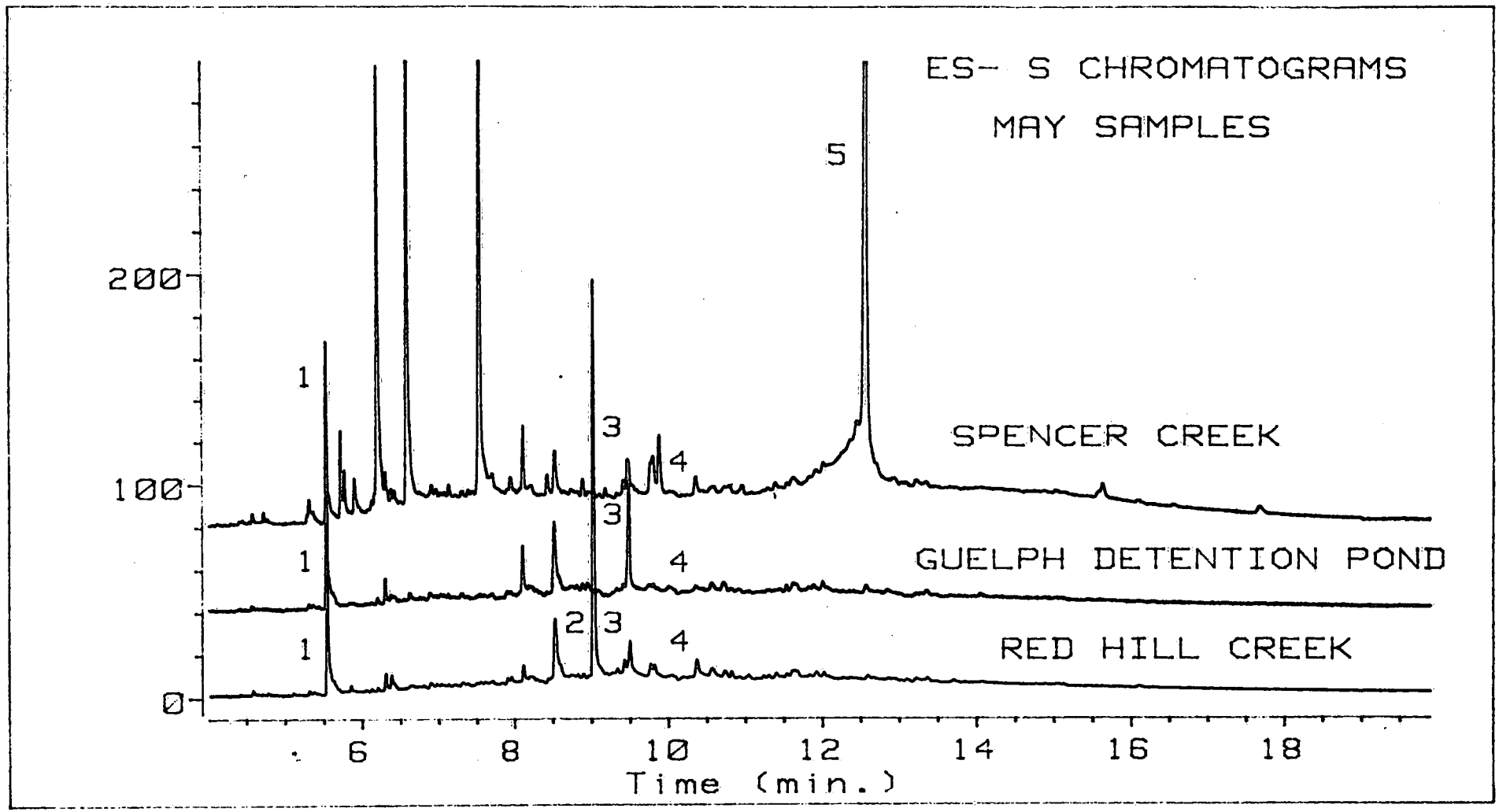
140
120
100
80
60
40
20
(x)
(z)
(y)
(q)
C
O
6
8
10
12
14
16
18
20
Time (min.)

FIGURE 2(b).


ES- S CHROMATOGRAMS
MAY SAMPLES
SPENCER CREEK
GUELPH DETENTION POND
RED HILL CREEK
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100
0
1
2
3
4
5
6
8
10
12
14
16
18
Time (min.)

FIGURE 3(a).

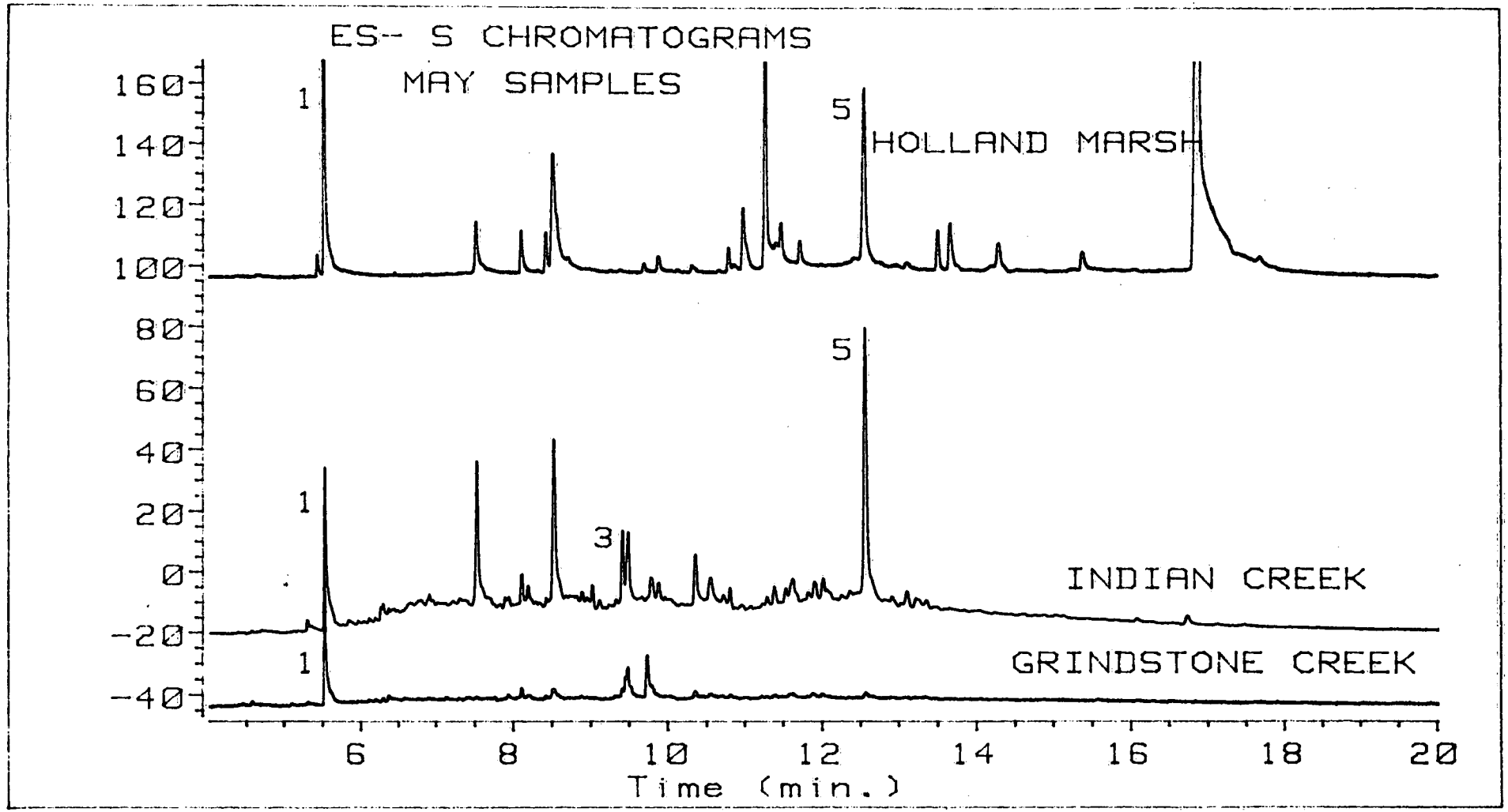

ES-- S CHROMATOGRAMS
MAY SAMPLES
160
140
120
100
80
60
40
20
0
-20
-40
1
5
HOLLAND MARSH
5
1
3
INDIAN CREEK
1
GRINDSTONE CREEK
6
8
10
12
14
16
18
20
Time (min.)

FIGURE 3(b).

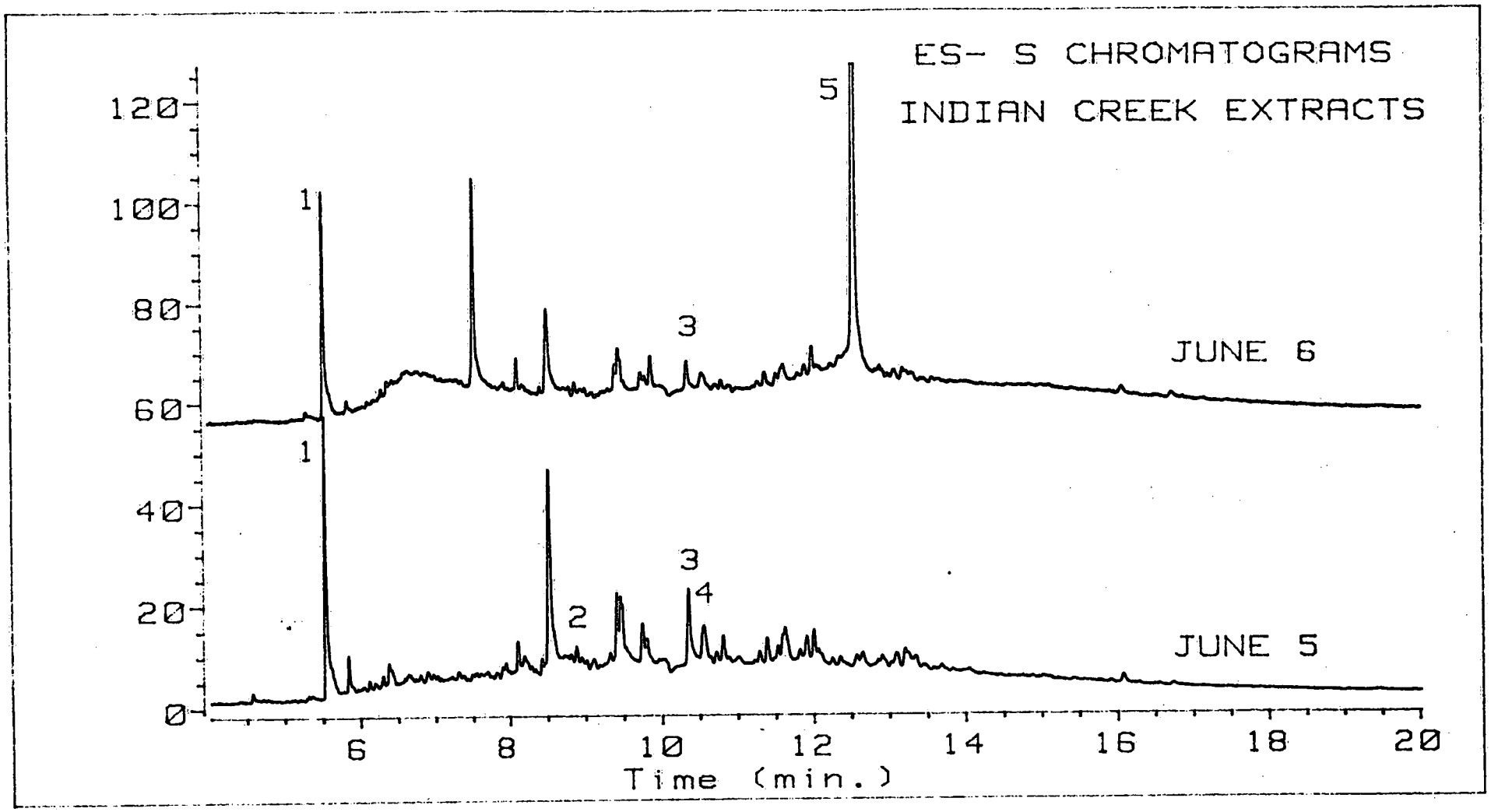

ES- S CHROMATOGRAMS
INDIAN CREEK EXTRACTS
JUNE 6
JUNE 5
1
2
3
4
5
120
100
80
60
40
20
0
6
8
10
12
14
16
18
20
Time (min.)

FIGURE 4.

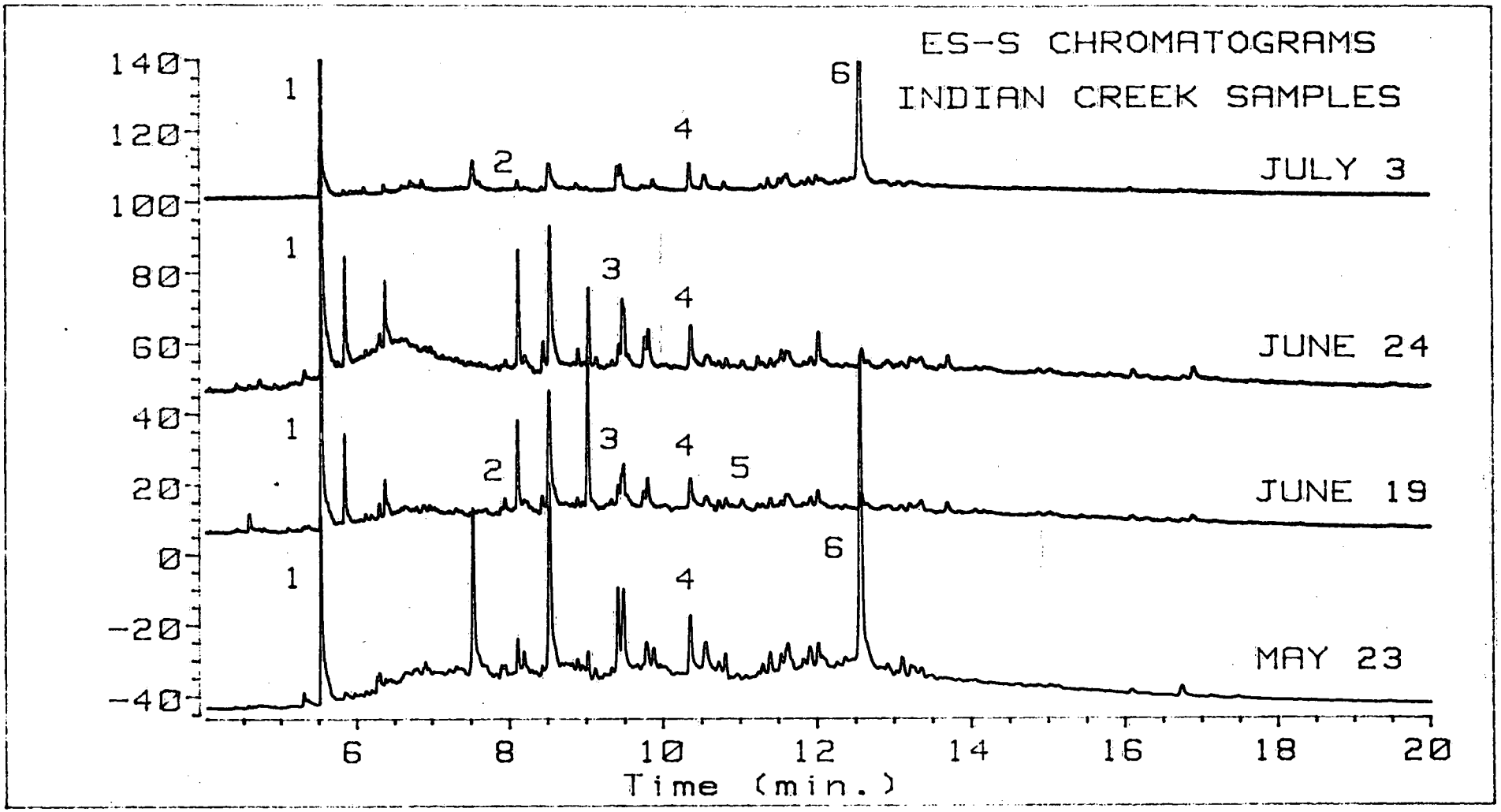
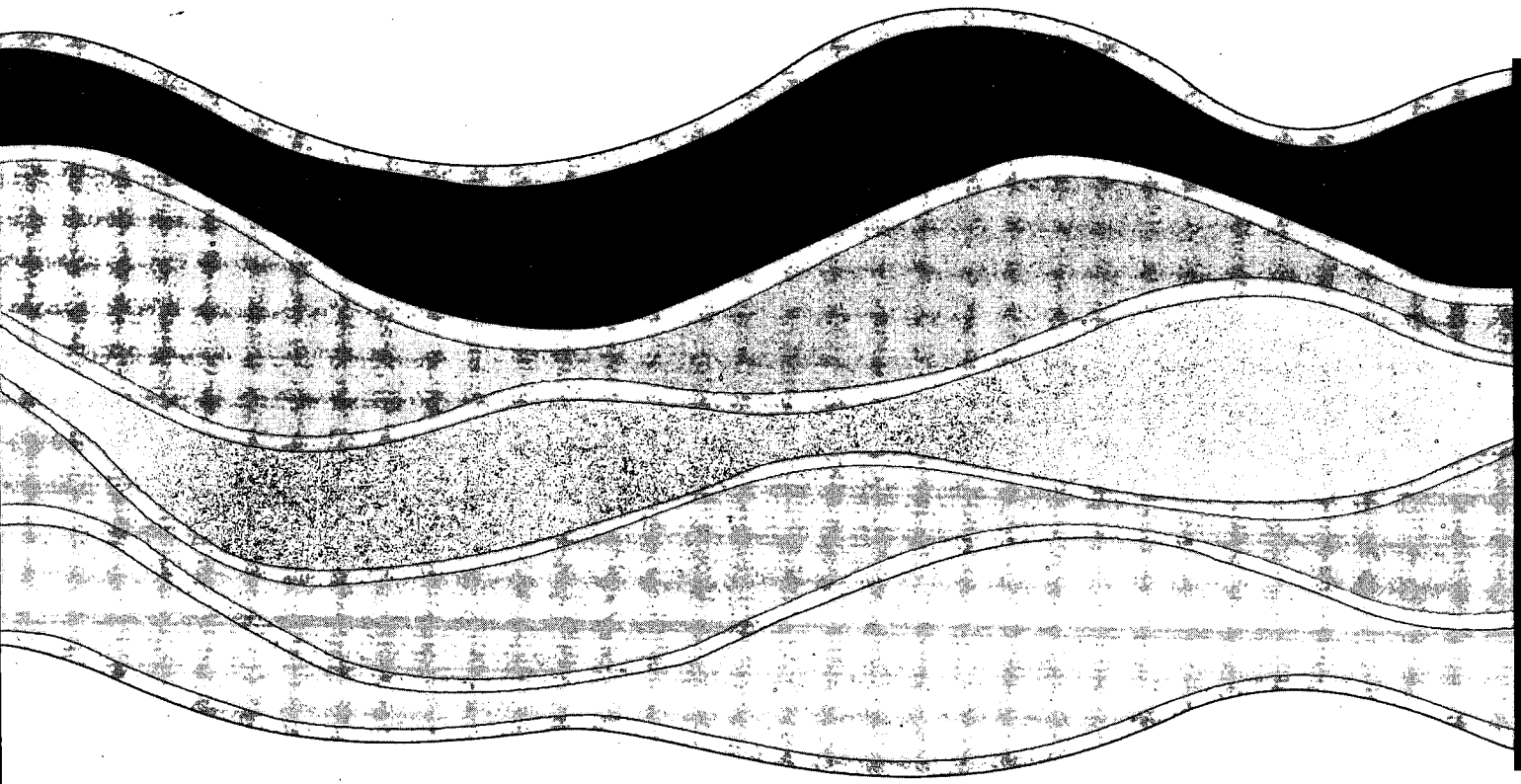

ES-S CHROMATOGRAMS
INDIAN CREEK SAMPLES
JULY 3
JUNE 24
JUNE 19
MAY 23
140
120
100
80
60
40
20
0
-20
-40
6
8
10
12
14
16
18
20
Time (min.)

FIGURE 5.



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