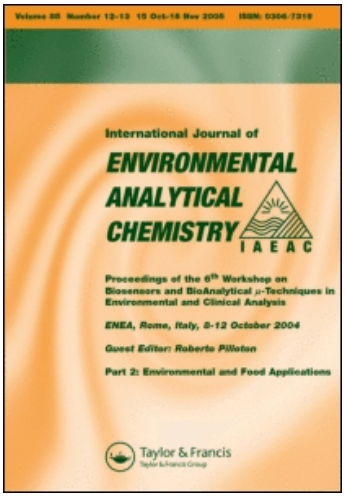

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A New Technique for the Rapid Analysis of Soil for the Presence of Polychlorinated Biphenyls

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A New Technique for the Rapid Analysis of Soil for the Presence of Polychlorinated Biphenyls

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A new technique for rapidly screening for the presence of PCBs in soil has been developed and tested in a field monitoring situation. The technique employs an atmospheric pressure chemical ionization mass spectrometer system mounted in a van to provide on-site mass spectrometric identification and quantitation of the compounds. A small soil sample is heated in a flowing stream of pure nitrogen, and the vaporized material is trapped on an adsorber which is thermally desorbed into the ion source of the mass spectrometer. A detection limit of approximately 1 μg/g of Aroclor 1254 has been achieved, with a total analysis time per sample of approximately 5 minutes. The process makes possible the direct analysis of soil samples without any chemical workup or preseparation.

INTRODUCTION

Few analytical systems are designed to accept the direct introduction of raw environmental samples for the detection of chemical pollutants in trace amounts. Complex workup procedures are usually required to prepare the sample for analysis. Consequently, there is often a long delay between sample collection and the receipt of the results of the analysis, which is usually performed using a combination of wet chemical and sophisticated instrumental procedures in a laboratory remote from the sample location. The

logistical problems encountered in handling large numbers of samples off-site and the lack of timely results which could be used to direct the on-going sampling program generally limit the scope of any study. Although there is increasing recognition of the necessity to develop rapid analytical techniques for use in the field, the major thrust of improvements in instrumentation and analytical techniques has in fact been directed towards obtaining higher sensitivity, specificity and accuracy, often with attendant increases in the complexity of the analysis. There are, however, numerous routine and emergency situations where the immediate acquisition of the results is a primary concern, and where the requirement for accuracy can be lowered in favor of increased speed. Cleanup operations, routine monitoring programs and investigations to determine the gross extent of environmental contamination can all benefit from analyses performed at the site that provide immediate results. For the past three years, a commercial atmospheric pressure chemical ionization/mass spectrometer (APCI/MS) system (the TAGA™) installed in a van has been used for the in situ and real-time analysis of air for trace organics.[1,2] The investigations have demonstrated the utility of obtaining the results in real time, and it has become apparent that a need exists for a system which can provide a similar type of rapid, on-site screening for contaminants in soil and water.

This paper describes a technique which was developed for the direct analysis of polychlorinated biphenyls (PCBs) and trichlorobenzene (TCB) in samples of clay soil using a mobile atmospheric pressure chemical ionization mass spectrometer system (a TAGA™ 2000), located at the site of a large spill of transformer fluid (the results of the analysis are reported in more detail in Reference 3). The sampling program was aimed at delineating the three-dimensional pattern of contamination in the soil around the site, as well as investigating migration pathways. The goals for the technique were that it be rapid, (10 to 20 samples per hour), that it be capable of detecting levels of about 1 microgram per gram of soil (μg/g), and that it be capable of handling small soil samples. The latter was required so that good spatial resolution could be obtained for studies of the migration pathways in the fractures. Because the main goal was to define the extent of soil contamination, and not to provide information for regulatory purposes, precision was more important than accuracy. An approximate measurement of the concentration of PCBs or TCB in a soil sample was acceptable as long as it was reproducible.

EXPERIMENTAL

Atmospheric pressure chemical ionization

The atmospheric pressure chemical ionization mass spectrometer system used in this study was a commercially available unit, the TAGA™ 2000. The system

is mounted in a van to provide mobility in a configuration described in a previous paper.[2] Sample molecules are introduced into the ion source in a stream of carrier gas, and react with ions generated from an atmospheric pressure corona discharge. The ions are sampled through a small orifice into the vacuum chamber (cryogenically pumped) and analyzed with a quadruple mass spectrometer. Ambient air can be drawn through the source at flowrates of one to two liters per second, in order to minimize sample loss on the walls of the glass tubing. Detection limits for a wide variety of organic and inorganic vapours in air are in the parts-per-billion to parts-per-trillion range.[1] For example, PCBs have been measured in ambient air and in stack gas from a cement kiln at the ng/m^3 level and the μg/m^3 level respectively.[4]

Previous analyses have used charge transfer from $C_6H_6^+$ to detect PCBs.[4] For the application described here, where it was necessary to ionize both PCBs and trichlorobenzene (TCB), hexafluorobenzene (IP = 10.0 eV[5]) was used as the reagent ion. Figure 1 shows a mass spectrum of the vapour above a surface of Aroclor 1254 (a mixture of PCBs), obtained with $C_6F_6^+$ as a reagent. The spectrum is weighted toward the more volatile components, since this is a headspace vapour analysis. The spectrum is consistent with our experience that only molecular ions M^+ are produced in the atmospheric pressure charge transfer process, and it reveals the distinctive chlorine isotope pattern for each species. The chemical ionization does not differentiate between different isomers; in general, experience has shown that all PCBs with the same number of chlorine atoms react similarly, so that the analysis generates a measurement of total monochlorobiphenyl, total dichlorobyphenyl, etc.

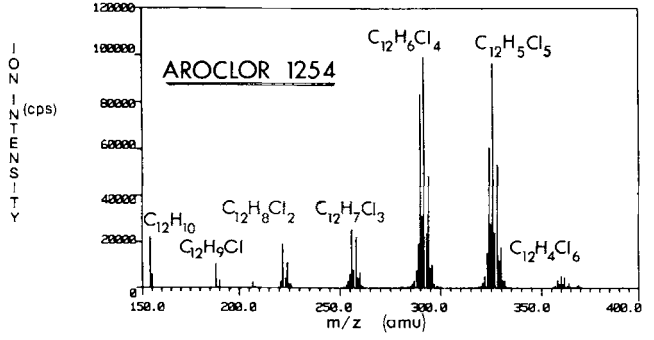

FIGURE 1 $C_6F_6^+$ charge transfer mass spectrum of the vapour phase above Aroclor 1254.

Analytical procedure

A small plug of soil, about 1.5 cm long and 0.3 cm in diameter (a "minicore") is placed directly in a small coil of Nichrome heating wire which is suspended in

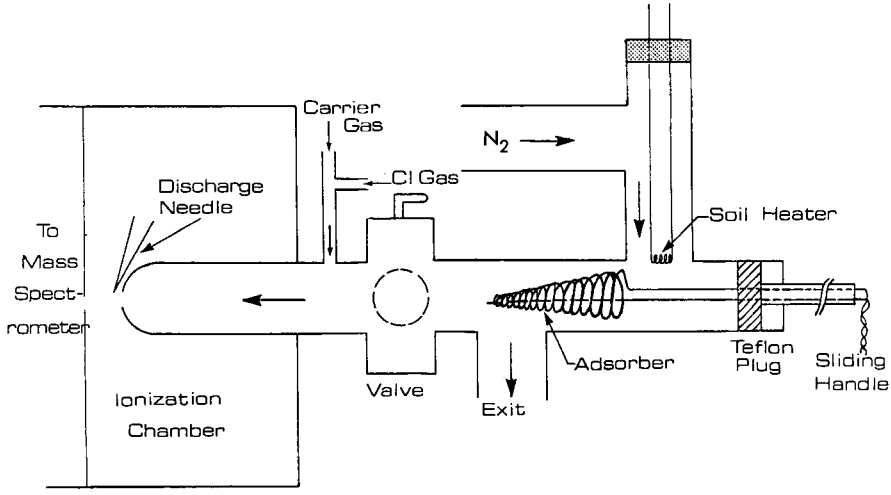

FIGURE 2 Soil minicore analysis inlet system, showing the soil heater and adsorber in the "collect" position. The adsorber is moved into the inlet tube, leading to the ionization chamber, by opening the valve and sliding the teflon plug forward in the line until it contacts the end surface of the valve.

the 22 mm glass inlet line (see Figure 2). The soil plug is heated by passing a current through the wire, thermally desorbing organics and water into a stream of pure nitrogen which passes over a conical wire coil located just downstream of the sample. This wire coil is approximately 4" long and 1/2" across at the base, and is coated with a thin layer of OV-17 which traps the less volatile organics such as PCBs and TCB. It is supported on a teflon plug, which can be moved in the glass line by means of an extended handle. In the sampling position (shown in Figure 2), the ionization chamber is isolated from the sampling line by a nylon stopcock valve. After the soil core has been fully desorbed (one minute) the valve is opened and the adsorber is moved forward into the ionization chamber where it is situated in the flow of carrier gas containing the reagent (C_6F_6). In this position the teflon plug separates the ionization region from the sampling line. A current is passed through the wire (adsorber), heating it to about 200°C in sixty seconds, and driving off the trapped species into the carrier gas, which flows into the reaction region. The bakeoff cleans the adsorber for another cycle. Single ion monitoring at the mass of interest followed by integration of the area under the curve allows quantitation of the amount of the compound on the coil. Alternatively, repetitive scans over a 10 to 15 amu interval during the desorption allows the nature of the major chemicals to be examined in terms of isotope patterns. After the sixty second desorption, the adsorber is returned to the sampling

position and a new minicore is inserted into the soil heater. The total sequence requires about three minutes. In a field situation, approximately 12 samples per hour can be analyzed, including the appropriate blanks and standards.

Although in principle the soil minicore could be heated in the inlet line with the desorbed material being carried directly into the ionization chamber, the use of the adsorber and separation of the sampling position from the ion source allows the ion chemistry to be optimized to reduce interference from other compounds. In our case, the water which evaporates from the wet soil can interfere with the analysis, so that the pre-separation of the organics from the water is a necessary first step.

Sampling procedure

The sampling procedure was intended for use in the analysis of samples obtained and brought to the instrument by individuals with little experience in the care required in sampling for trace organic chemicals. It was thus necessary that the sampling technique minimize the possibility of cross-contamination due to either handling error or sampling error. The approach chosen involved the preparation of minicores of soil in 6 mm pyrex tubing. Large cores of clay (7.6 cm by approximately 50 cm obtained by boring at the site) were broken to reveal two fresh faces. Pyrex tubes 6 mm in diameter were then pressed lightly into the face at 6 to 10 random locations (at least 1/2″ from the edge) to form composite 0.3 × 1.5 cm long cylindrical samples. Alternatively, loose soil was moulded into cylindrical samples with the tube. This sampling technique is applicable only to relatively moist samples that retain their shape when the sample is extruded from the glass tube. In practice, each core is extruded with a glass rod which fits snugly into the tube. The intact core is pushed directly into the soil heater without any additional handling which could lead to sampling error. Both sample tube and rod are used only once and then discarded. We find that the technique can be used in the field with a minimum chance of error, since only the inner surface of the tube is ever in contact with the soil. Additionally, the ends of the cores can be broken off and discarded as another precaution. This was standard practice in the field study.

The soil sits directly in the soil heater during the desorption step, so that there is no contact with the glassware in the desorption system. The soil heater wire reaches a temperature of several hundred degrees during the heating cycle, sufficient to eliminate carry-over on the surface of the wire from one sample to the next. Figure 3 shows the response to a 500 μg/g standard followed by a soil blank, demonstrating the virtual absence of a memory effect at this concentration. For much larger concentrations (5000–20,000 μg/g), some residual response is visible during the subsequent one or two blank injections, and it is therfore necessary to introduce a blank after a very contaminated sample.

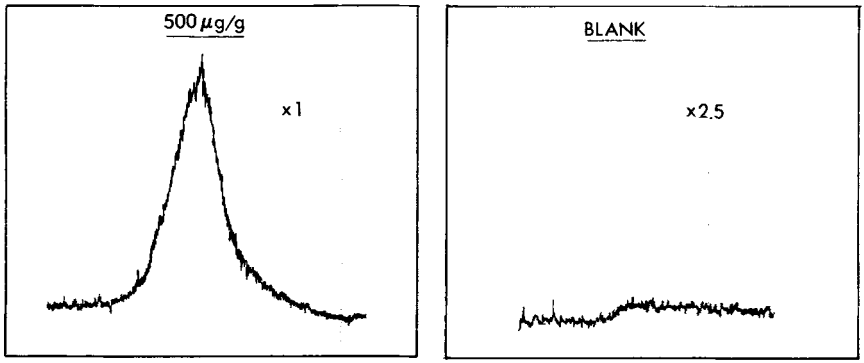

FIGURE 3 Response curves (ion current vs time) at m/z = 326 for a 500μg/g PCB standard soil sample and for a blank soil sample analyzed immediately after. Note the change in scale for the blank.

Preparation of standards

Calibration of the system for the response to PCBs and TCB was based on the introduction of known homogeneous mixtures of clay, water, Aroclor 1254 and TCB. Clean, dry clay (Wyoming Bentonite supplied by Agriculture Canada) and solutions of Aroclor 1254 and 1,2,4-trichlorobenzene in hexane (pesticide grade from Fisher Chemicals) were mixed to form a slurry, wetting the soil completely. The Aroclor 1254 was a U.S. Food and Drug Administration Standard, and the 1,2,4-trichlorobenzene (99% pure) was obtained from RFR Corporation, Hope, RI. The hexane was evaporated from the slurry at room temperature until the clay was dry (requiring about 15 minutes in a fume hood). Distilled water was added (1 g of water to 1 g of soil) and mixed to form a thick paste. Blanks were prepared by following the same procedures but without adding PCBs or TCB. The standard soil samples, prepared in concentrations from 1 μg/g to 20,000 μg/g (weight of compound/weight of wet soil) of Aroclor 1254 and TCB, were stored in glass jars sealed with aluminum foil and screw-top lids. All glassware was throughly cleaned with pesticide grade acetone and oven dried at 150° before use.

RESULTS AND DISCUSSION

Calibration

The response of the system to TCB was quantitated by monitoring the ion current at m/z = 180 while the adsorber was heated. This mass corresponds to the isotomer containing three ^{35}Cl atoms, which constitutes 43.0% of the total. The other isotomers are in the ratio m/z = 180/182/184/186 = 100.0/97.5/31.7/3.4. PCBs were measured by monitoring m/z = 326, the

most abundant of the six isotomers of pentachlorobiphenyl. The pentachlorobiphenyl component of Aroclor 1254 was chosen as the tracer because (a) it is the most abundant component of Aroclor 1254, constituting about 48% of the total;[6] (b) it is less readily biodegraded than the tri- and tetrachlorobiphenyl components;[6,7] and (c) it is more volatile than the hexachlorobiphenyl component (which is even more stable against biodegradation).

The use of pentachlorobiphenyl as a measure of the total amount of Aroclor 1254 is suitable for screening purposes, where knowledge of the relative concentrations of the PCB components is not important. However, it should be pointed out that pentachlorobiphenyl is a major component in Aroclor 1248, Aroclor 1254 and Aroclor 1260. If no measurements of other homologues are made, field measurements in an unknown situation would have to be viewed as representative only of the level of pentachlorobiphenyl in the soil. For the purpose of the particular field program for which this technique was developed,[3] where there was foreknowledge of which PCB formulation had been in use at the plant, the assumption was made that within the limits of accuracy required, the level of pentachlorobiphenyl directly reflected the level of Aroclor 1254. All measurements therefore were reported as equivalent Aroclor 1254 concentrations, using the soil spiked with Aroclor 1254 for calibration. Support for the above mentioned assumption comes from gas-liquid chromatography (GLC) measurements which in the majority of instances, showed PCB patterns in the soil similar to that of Aroclor 1254.[3] In such cases, there was little depletion of the pentachloro components relative to the others. For greater resolution of the composition, the mass spectrometer could have been programmed to examine several components simultaneously.

The one-minute heating cycle for the desorption of the integrator produced symmetrical peaks in the case of both PCBs and TCB. The heights of the peaks were related to the concentrations in the sample, and plots of the peak height versus the concentration (Figures 4 and 5) show useful linearity at concentrations up to 1000 μg/g. Some curvature is observed with PCBs at concentrations above about 1000 μg/g and with TCB above about 500 μg/g. Although a non-linear calibration equation could be developed for quantitation, a single response factor, i.e., a linear response curve is satisfactory for rapid screening at concentrations below about 1000 μg/g.

Another method was investigated for use with highly concentrated samples. Instead of using a heating cycle during the desorption of the integrator, the coil was simply placed in the stream of carrier gas entering the ionization chamber. With high concentrations, the rate of desorption from the collector at room temperature is sufficient to produce a measurable increase in the ion current. This response showed a useful concentration/response relation in the range of 500 to 10,000 μg/g, and allowed the concentration of PCB and TCB even in

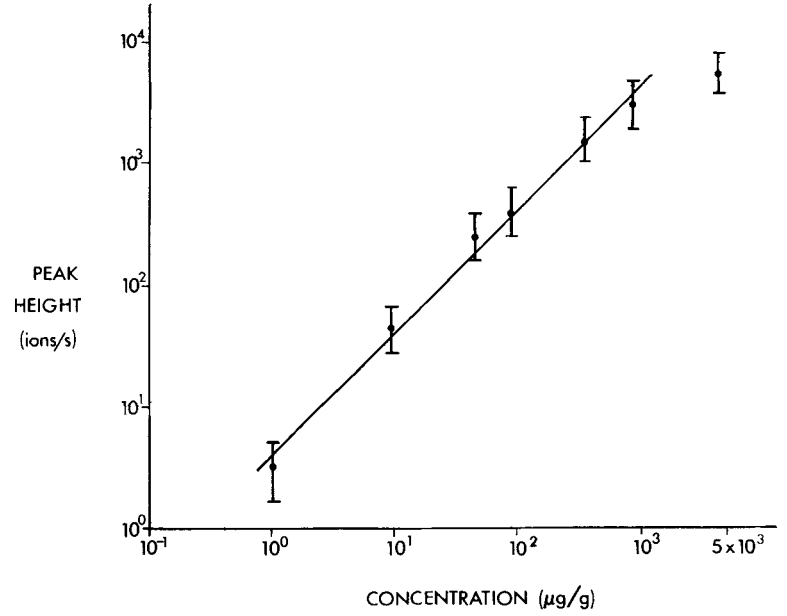

FIGURE 4 Peak height (at m/z = 326) vs concentration of Aroclor 1254 in the soil.

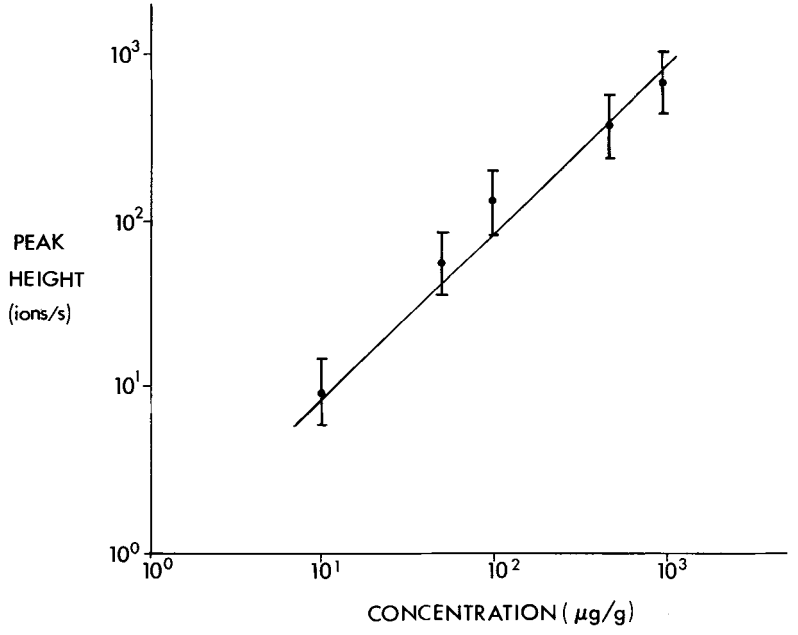

FIGURE 5 Peak height (as m/z = 180) vs concentration of TCB in the soil.

highly contaminated soils to be estimated. Occasionally, when a field sample was highly contaminated with other pollutants which interfere with the analysis due to competition for the reagent ion, quantitation was performed by spiking the actual sample with a known amount of Aroclor 1254. In the field, this constant addition method gave a practical and useful method for estimating the Aroclor 1254 concentrations in these situations.

Precision and accuracy

The attainment of acceptable precision for the minicore analysis technique depends in part upon the analyst obtaining uniform core lengths. The precision of the sampling procedure was tested independently by loading ten minicores under the same conditions which would be used during an actual field analysis program. The average weight of the ten samples was 0.18 g and the relative standard deviation was 8%. This shows that reasonable precision can be obtained by an operator exercising sufficient care. The overall precision of the measurement of concentrations in the soil was tested by repeated introductions of a 10 μg/g PCB standard. A total of nine measurements showed a relative standard deviation of 22%; the analytical precision in a field situation, with a standard introduced after every 10 samples and after every major change in the contamination level in the samples, is therefore estimated to be better than 30%. This is sufficient analytical precision to permit the geologist to examine soil heterogeneity and its relation to specific migration pathways. The information on small scale variations which is diagnostically useful for investigating migration mechanisms is lost in GLC techniques due to the requirements for larger samples.

The requirements for accuracy are lower than those for precision, as discussed previously. The accuracy depends not only on the accuracy of the prepared standards, but also on how closely matched are the physical and chemical properties of the standard soil to those of the unknown sample. Factors which were examined for thier possible influence on the quantitation include soil composition, density and water content. The clay used in the preparation of the standards was Wyoming Bentonite, a montmorillonite. In the field study, Regina Clay, also a montmorillonite, was spiked with 10 to 100 μg/g of PCB, and the responses compared with the responses from similar standards prepared from Wyoming Bentonite. The responses of the two soils differed by less than 20%, within the limits of precision of the technique, so that there was no evidence of a systematic difference between the soils.

Since constant volumes of soil are analyzed, quantitation of the contaminants relative to the weight of the wet soil relies on the density of the standard being equal to the density of the samples. The density of the standards (at 50% water content) was 1.3 ± 0.2 g/cc, while the typical density of field samples (of about 20% water content) is between 1.2 and 1.4 g/cc. In

situations where the sample density is different on average from that of the standard, a simple correction factor of the ratio of the two densities could be applied to the results if greater accuracy is required.

Standards were prepared with a moisture content of 50% by weight since this was the minimum moisture required to produce a core which would remain intact when extruded. No major differences were noted in the response when the standards were compared to materials containing 70% water. Additionally, comparison of the analysis of field samples containing about 20% water with the results of the same samples analyzed by classical extraction and gas chromatography techniques did not indicate any difference of sufficient magnitude to affect the usefulness of the technique for the intended purpose (Table II). Conceivably, problems might be encountered with particularly dry soils. This point was not addressed in this study.

Comparison of sampling methodology and analytical techniques

Early in the development program it was recognized that the minicores could be prepared either as a composite of small cores or as a single intact 1.5 cm core obtained from one location on the sample surface. Because the emphasis of the technique was on the rapid screening of a large number of samples to provide an overall large scale picture of the contamination pattern at the site of the spill, the two techniques were examined on samples of contaminated clay taken from the actual site in Regina, Saskatchewan.[3] The results of the single core samples shows that the distribution of PCBs across the faces of the large cores which are broken open can be (as might be expected) very heterogeneous—some locations on a fracture surface have less than 1–20 μg/g and others on the same surface contain more than 50–500 μg/g. Table I does show that all composite samples on a fracture surface evidence of PCBs, suggesting that the composite technique has a higher probability of detecting PCBs on a contaminated fracture surface than the technique involving a single core.

In parallel with the APCI/MS screening analysis, some duplicate samples were obtained, sealed and stored on ice for later analysis by gas-liquid chromatography (GLC). A representative selection of the results of this comparison is shown in Table II, which lists the range in concentration found in three minicores taken from the same core face for several samples, and the corresponding concentration found by GLC analysis of an extract of 20 grams of homogonized soil taken from the same location. What is wanted in a screening technique of the nature which has been described, is that there be a consistent and informative correlation between the patterns revealed by the two techniques. Examination of the results shows a highly useful correlation

TABLE I

A comparison of sampling methods in three different soil faces. "Single" refers to the technique of obtaining a mini-core from one location on the surface. "Composite" refers to obtaining a composite mini-core, as described in the text

Hole number	Sample number	Concentration (μg/g)	Sampling method
Core 1/Face 1	1	<1	Single
	2	<1	Single
	3	50–100	Single
	4	<1	Single
Core 2/Face 1	1	700–1500	Composite
	2	<10	Single
	3	<20	Single
	4	50–200	Composite
Core 2/Face 2	1	50–200	Composite
	2	300–600	Composite
	3	500–1000	Single
	4	<20	Single
	5	300–600	Single
	6	<20	Single

TABLE II

Comparison of residue patterns revealed by GLC and by APCI/MS analysis

Sample[a]	Moisture Content (percent)	Concentration of Aroclor 1254 (μg/g)	
		GLC[b]	APCI/MS[c]
A	20	$6–7 \times 10^3$	$0.6–2 \times 10^3$
B	23	4×10^3	$0.6–4 \times 10^3$
C	26	2×10^3	$0.6–2 \times 10^3$
D	22	1×10^3	$0.6–1 \times 10^3$
E	23	7×10^2	$2–5 \times 10^3$
F	26	1×10^3	1×10^3
G	24	20	20–60
H	23	8	<10[d]
I	22	1	<10[d]
J	25	1	<60[d]
K	22	0.3	<2[d]

[a]7.6 cm × 22 cm cores of clay were obtained from two sampling sites at various depths.

[b]Concentrations of Aroclor 1254 measured by extraction of 20 g of clay from the core, followed by GLC analysis. Aroclor 1254 was used as a standard and no correction was made for profile matching. Complete results reported in Reference 3.

[c]Results from duplicate core samples, analyzed by APCI/MS as described in this paper. Complete results reported in Reference 3.

[d]Detection limits varied due to interference of other chemicals at the site.

between the contamination patterns revealed by the rapid screening technique and the more conventional slower technique involving GLC analysis. As has been emphasized by Roberts *et al.*,[3] it is not the results of a single sample that is of importance, but the general pattern which appears from examining the results as a whole. The upper range on the results obtained with the APCI/MS technique are generally within a factor of two of the results of the GLC analysis. Differences of a factor of two or three are not unexpected in view of the widely different sample sizes analyzed by the two techniques, and the observed inhomogeneity of the samples. This degree of correlation is well within the range needed for screening purposes. At high concentrations the GLC results tended to be higher than the TAGA™ results; however, whenever the GLC analysis suggested that the concentrations were below the detection limit of the APCI/MS technique, the results were consistent. Field experience has shown[3] that the detection limit of the system can vary when the soil is highly contaminated with other compounds which interfere in the ion chemistry (other aromatic hydrocarbons, for example). In general, however, detection limits of 1 to 20 μg/g were achieved during the field program.

Since the TAGA™ was originally developed as a trace gas analyzer, and has been previously used for the direct detection of PCBs in ambient air, a possible technique involving the direct sampling of the air above a contaminated surface was briefly studied. The preliminary results showed promising response characteristics for the technique. The signal was proportional to the concentration at the surface of the soil for PCB levels in the 500–5000 μg/g range and for TCB in the 100 to 1000 μg/g range. This approach was not further pursued because of time constraints, and was not used in the field study. However, it could prove to be an extremely rapid method for screening large areas for high levels of contamination.

CONCLUSIONS

The technique of heating a small core of soil in a carrier gas stream to volatilize the compounds from the soil for analysis by APCI/MS provides a method for rapidly screening soil samples for PCBs and TCB, and is potentially useful for the detection of other involatile organics in soil. Detection limits in the range of 1 μg/g have been achieved for PCBs in soils which do not contain high levels of interfering contaminants. In highly polluted field samples, detection limits in the 10–20 μg/g range can generally be obtained. The procedure is rapid enough to be useful on-site during a monitoring program and sensitive enough to be analytically useful in clean-up investigations. The accuracy is sufficient for the intended purpose of the rapid delineation of contamination patterns. The technique has been successfully tested on a montmorillonite (Regina clay) during a field program, and with careful calibration, should find application

for other environmental contaminants in other low organic soils. The applicability of the technique to high organic soils would need to be tested. It is known that PCBs adhere strongly to organic materials[8,9,10] and it is conceivable that the heating cycle would have to be modified. The technique used in the actual sampling can be used by relatively inexperienced field crews with a minimum of training.

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