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ANALYSIS OF SOILS AND SEDIMENTS
FOR ORGANIC POLLUTANTS

by

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SUMMARY

Twenty soil samples have been analysed for their content of organic pollutants using either selective ion recording (SIR) or full scan mass spectra. 4 soils and 2 sands showed levels of one or two groups of PCBs slightly in excess of the detection limit, one sample showed a similar level of 2,4-D and 3 samples contained dieldrin at or just above the detection limit.

Aldrin, endrin, 2,3,7,8-tetrachlorodioxin, 2,4,5-T, pentachlorophenol and hexachlorobenzene were not detected in any samples.

Although lindane, endosulphan, pp-DDT, fenitrothion, malathion, parathion, 1,4-dichlorobenzene, trichlorobenzene and hexachlorobutadiene were not detected in any sample, the results must be treated with caution as there is the possibility of loss associated with high volatility or with the treatment prior to measurement.

Polycyclic aromatic hydrocarbons and alkyl naphthalenes are present in high abundance in several sediments. Fluoranthene showed an abundance varying from 20-5100 ng/g. The presence of $\alpha\beta$ -hopanes and n-alkane distributions characteristic of petroleum pollution is reported.

Background

20 samples of soil or sediment (7 of which were predominantly sand) from various locations were received for analysis of their content of organic pollutants. These analyses were performed using a capillary column gas chromatograph equipped with an electron impact (E.I.) mass spectrometer as detector and using computerised data storage. The instrument was calibrated with each target compound to determine its retention time, and the most suitable ions in full scan mass spectra were identified for use either in selective ion recording (S.I.R.) or to detect the possible presence of target compounds in full scan mass spectral data.

In addition to the target compounds, the full scan data were examined to determine the composition of natural organic products and a series of diagnostic fragment ions was used to search for additional anthropogenic products.

Organic-rich environmental samples are notoriously difficult to analyse for pollutant organics owing to the presence of high concentrations of many natural organic compounds. A single procedure for extraction and clean-up was adopted. It was designed for chlorinated aliphatic and aromatic hydrocarbons and other pesticides containing acidic functional groups and was based on published methods for the determination of organic pollutants in soils and sediments (Nash *et al.*, 1986, Lopez-Avila *et al.* 1989; Garrigues and Bellocq, 1989; Stan, 1989).

Methodology

The chosen method of analysis of the target compounds was capillary column gas chromatography using a mass spectrometer operating in the E.I. mode as detector (GC-MS).

The highest detection sensitivity is obtained by selective ion recording (S.I.R.) of intense ions specific to individual target compounds. Using this technique only selected ions are monitored during the GC-MS run. The longer scanning time for each ion, compared to full scan acquisition, gives improved sensitivity, typically by a factor of 30-40 as used in the present study. On the debit side, more general mass spectral information about the eluted peak is lost. For chlorinated aromatic hydrocarbons the selected ions are usually molecular ions M^+ or $(M-Cl)^+$ ions, thus giving high selectivity. For aliphatic compounds ions of low mass are predominant and are thus less specific.

The number of ions monitored is constrained by the need to obtain 8-10 scans across each GC peak. A suite of 10 ions was monitored using a dwell time of 80 milliseconds per ion. The technique is particularly useful for targets consisting of a large number of isomeric compounds, such as PCBs (and Dioxins), not all individually available but eluting in a region defined using commercially available mixtures.

Target compounds

The target compounds used to establish an extraction and clean-up procedure were:

- (a) 2,4-Dichlorophenoxyacetic acid (2,4-D)
- (b) 2,4,5-Trichlorophenoxyacetic acid (2,4,5-T)
- (c) Pentachlorophenol (PCP)
- (d) Dieldrin
- (e) Polychlorinated biphenyls (PCBs)
- (f) Dioxins

While (a) - (d) are individual compounds, it should be noted that (a), (b) and (c) require suitable derivatization for GC-MS analysis. The clean-up procedure for the sediment extracts (see below) was designed to produce suitable derivatives.

Targets (e) and (f) are complex mixtures in which a single mass ion may be used to characterize each group containing the same number of chlorine atoms. PCBs contain up to 10 chlorine atoms and have great structural complexity; 209 compounds are possible. Environmentally significant PCBs usually contain 3-8 Cl atoms, together comprising 190 congeners.

Dioxin derivatives contain up to 8 Cl atoms, totalling 75 congeners; previous studies on sediments have found octachloro-dioxin to be the dominant compound, together with less chlorinated analogues. In this work only 2,3,7,8 - tetrachlorodibenzo-p-dioxin (TCDD) was measured. This is the most important TCDD isomer in terms of regulatory emphasis, and is commonly the only dioxin isomer measured in environmental pollution studies.

Target compounds in groups (d)-(f) were measured by SIR throughout. Targets (a) and (c) were determined either by SIR or from full scan data; the latter method was used for target (b).

The following ions were used for SIR detection:-

Compound	Ion (m/z)	Structure
2, 4-D Methyl ester	199	[M-Cl] ⁺
PCP Methyl ether	265	[M-15] ⁺
Dieldrin	79	Not known (see note 1)
Trichloro biphenyls	256	M ⁺
Tetra " "	292	M ⁺
Penta " "	324	M ⁺
Hexa " "	360	M ⁺
Hepta " "	394	M ⁺
Octa " "	430	M ⁺
2,3,7,8-Tetrachlorodioxin	322	M ⁺
Aldrin	263	M-99
pp-DDT	235	M-117

Note 1. The full scan mass spectrum of dieldrin shows no intense ions about m/z 100, so the base peak is used. This low mass ion is relatively unspecific, however the compound elutes close to the internal standard.

Additional targets were:-

- (g) Chlorinated aliphatics :- Lindane, Aldrin, Endrin, Endosulphan, Hexachlorobutadiene.
- (h) Chlorinated aromatics :- 1,4-Dichlorobenzene, Trichlorobenzene, Hexachlorobenzene, pp-DDT
- (i) Organo-phosphorus esters :- Fenitrothion, Malathion, Parathion.
- (j) Anthracene.

Targets in groups (g)-(j) were searched for using full scan acquisition alone, except for Aldrin and pp-DDT in a few samples, for which SIR was used.

The organo-phosphorus esters, lindane, endosulphan and pp-DDT were found to be degraded during hydrolysis as described below, but a degradation product from each target, except lindane and endosulphan, could be identified from full-scan mass spectra.

Environmental Samples

The samples fall into two groups differing greatly in organic content:

- (a) 11 Soils and 2 sediments relatively rich in organic matter.
- (b) 7 Sandy sediments very low in organic matter and extractable material.

The abundance of natural organic products affects the detection limits of the target compounds, as determined by a series of experiments in which samples were spiked with target compounds prior to extraction.

Extraction

The samples were air dried, passed through a 4 mm sieve to remove stones (glass in several cases) and plant roots. A weighed amount of sediment (50-70g, according to bulk density) was placed in a Soxhlet thimble, spiked with an internal standard (p-terphenyl-d¹⁴) and extracted with chloroform under reflux for 16 hours, with copper foil in the boiler flask to remove any elemental sulphur. The solution was filtered and evaporated to dryness.

Clean-up and Derivatisation

The crude product was dissolved in toluene:methanol (1:2) and hydrolyzed with aqueous KOH for 2 hrs. under reflux, to remove complex wax esters that are difficult to separate from the PCB target compounds by liquid chromatography and also cannot be eluted from the GC column. The hydrolysis mixture was diluted with water, acidified and then the products were extracted with ether. Free fatty acids were converted into methyl esters by treatment with diazomethane. The product was purified by Solid Phase Extraction (SPE) using a Florisil column. Diazomethane treatment will convert targets (a) and (b) into the analogous methyl esters suitable for GC, and converts pentachlorophenol into the methyl ether derivative, also suitable for GC.

A modified clean-up procedure was used for sand samples 38, 54 and 55 as results on the other sands showed a virtual absence of higher plant input to these samples, making the hydrolysis stage necessary. This modified procedure allowed direct determination of target compounds decomposed during hydrolysis, namely lindane, endosulphan, pp-DDT and the organo-phosphorous compounds (see Table 2).

The reference mixture of the target compounds di-, tri- and hexa-chlorobenzene and also hexachlorobutadiene contained such low levels of the latter two compounds that it was impracticable to add detectable amounts to sediments. Di- and tri-chlorobenzenes in this reference mixture could not be detected at 200 and 20 ng/g of organic sediment, respectively, probably because these compounds and also hexachlorobutadiene are more volatile than naphthalene, which could be detected in many sediments (see later section on Polycyclic Aromatic Hydrocarbons), but is probably not recovered quantitatively. The detection limit for hexachlorobenzene in full scan mode was estimated at 20 and 10 ng/g in soils and sands, respectively, by analogy with PCBs.

Results

The abundances of target compounds are shown in Tables 1 and 2. In addition to the environmental samples listed in Table 2, the remaining samples, which had been cleaned up using the hydrolysis procedure, failed to show detectable amounts of degradation products of fenitrothion, malathion and parathion. The higher detection limits of degradation products in hydrolysed extracts, compared with those of the parents in the unhydrolysed sediment extracts, reflect a low recovery of degradation products from chromatographic clean up using solid phase extraction.

The failure to detect 1,4-dichlorobenzene, trichlorobenzene and hexachlorobutadiene in any soil or sediment is attributed to their high volatility. Hexachlorobenzene could not be detected in any sample.

References

- Garrigues P. and Bellocq J. (1989), J. High Resolution Chromatogr. 12, 400-403.
Lopez-Avila V., Milanes J., Dodhiwala N.S. and Beckert W.F. (1989), J. Chromatogr. Sci. 27, 209-215.
Nash R.G., Wells M.J.M., Smith A.E. and van Wambeke E. (1986), Analytical Methods for Pesticides and Plant Growth Regulators, Vol. 15, 247-285.
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Appendix

During the study full scan mass spectra were obtained on the extracts studied by the SIR technique. The advantages of this are:-

1. To check the identity of peaks in the SIR traces, allowing one to eliminate non-chlorinated compounds which contain an ion of the same unit mass as that chosen for the target compounds.
2. To obtain additional information about the presence of other anthropogenic pollutants present in the samples.

Polycyclic Aromatic Hydrocarbons (PAH)

Full scan spectral data showed a series of PAH dominated by phenanthrene, fluoranthene and pyrene. Other PAHs, identified by co-elution with an authentic mixture and also by comparison of mass spectra with the NIH library of mass spectra, include benzofluoranthenes, benzopyrenes, indeno(1,2,3-cd)-pyrene and benzo(ghi)perylene. These PAH arise from combustion and are transported aeriually to environments remote from their source. Phenanthrene is always more abundant than anthracene, a target listed in table 1, as the latter linear fused ring system is less stable.

Some of the environmental samples also contain naphthalene and a homologous series of C₁-C₃ alkyl naphthalenes, identified by the NIH library. The source of these is not known by me, but it is evidently independent of the source of the more highly condensed PAH discussed above, based on the lack of correlation in abundance between fluoranthene, the dominant PAH, and the alkyl naphthalenes (Figs 1,2). The abundances of fluoranthene and the combined abundance of alkyl naphthalenes is given in Table 3.

Group (a) samples notable for high abundance of fluoranthene are 96 (Fig 1) and 97/100/118, however these two differ markedly in the relative abundance of alkyl naphthalenes. Sample 32/35 (Fig. 2) stands out for the high abundance of naphthalenes, which exceed fluoranthene even though the abundance of the latter is the third highest.

Other features from full scan spectra

The chain length distribution of sedimentary *n*-alkanes and fatty acids are broadly indicative of the organic source materials. Thus terrestrial input shows a dominance of C₂₅-C₃₃ alkanes and C₂₀-C₃₀ fatty acids, due to more rapid decay of C₁₆ and C₁₈ fatty acids under aerobic conditions. Aquatic biota show a predominance of C₁₅-C₂₃ alkanes and C₁₆ and C₁₈ fatty acids, including unsaturated fatty acids.

Soils/Organic Sediments

These generally contain *n*C₁₅-*n*C₃₃ alkanes in which there is a predominance of odd-carbon homologous above C₂₃, indicative of higher plant input (Fig. 3, upper). The most abundant compound is either C₂₉ or C₃₁.

Fatty acid methyl esters are the dominant constituents, ranging from *n*C₁₄ to *n*C₃₂ and showing a bi-modal distribution maximising at C₁₆ and either C₂₆ or C₂₈. Among these samples, 6/7/8, 32/35, 47/48/93 and 89/90/101/105 show a relatively higher abundance of C₁₆ and C₁₈ unsaturated constituents than the remaining samples.

Sandy sediments

n-Alkanes show a much lower terrestrial component (Fig. 3, lower), especially in samples 2⁴ and 5⁴, relative to shorter chain alkanes, than in the organic rich sediments. Fatty acid methyl esters show a dominance of the shorter chain members, C₁₆ and C₁₈, only sample 3 showing a bimodal distribution in which C₂₆ or C₂₈ is more abundant than C₁₆. Unsaturated C₁₆ and C₁₈ constituents are abundant, relative to the saturated homologues, except in sample 3. This sand sediment, therefore, is characterized by a relatively greater input of terrestrial organic matter than the other sands.

Table 1. Abundances of target compounds (ng/g sediment)

Sample	ALDRIN	ENDRIN ⁺	DIELDRIN	PCBs (no. of Cl atoms)						2,3,7,8 - DIOXIN	2,4-D	2,4,5-T ⁺	PCP	ANTHRACENE	pp-DDT [*]
				3	4	5	6	7	8						
<u>a) Soils/Organic</u>															
<u>Sediments</u>															
74,75,76.	<20 ⁺	<20	<5	<1	<1	<1	<1	<4	<4	<2	<15 ⁺	<15	<20 ⁺	140	<50 ⁺
6,7,8.	<20 ⁺	<20	<5	<1	<1	<1	<1	<4	<4	<2	<15 ⁺	<15	<20 ⁺	120	<50 ⁺
107.	<20 ⁺	<20	5	2	2	<1	<1	<4	<4	<2	<15 ⁺	<15	<20 ⁺	110	<50 ⁺
97,100,118.	<20 ⁺	<20	<5	<1	<1	<1	<1	<4	<4	<2	<5	<15	<20 ⁺	100	<50 ⁺
88,99,103.	<20 ⁺	<20	8	<1	<1	2	<1	<4	<4	<2	<5	<15	<20 ⁺	10	<50 ⁺
73.	<20 ⁺	<20	7	<1	<1	1.3	<1	<4	<4	<2	<5	<15	<20 ⁺	10	<50 ⁺
58.	<20 ⁺	<20	<5	<1	<1	<1	<1	<4	<4	<2	<5	<15	<20 ⁺	30	<50 ⁺
59.	<20 ⁺	<20	<5	<1	<1	<1	<1	<4	ND	<2	<5	<15	<5	<10	<50 ⁺
60.	<20 ⁺	<20	<5	<1	<1	<1	<1	<4	ND	<2	<5	<15	<5	<10	<50 ⁺
32,35.	<20 ⁺	<20	<5	<1	<1	<1	<1	<4	ND	<2	<5	<15	<5	110	<50 ⁺
96.	<20 ⁺	<20	<5	<1	<1	<1	<1	<4	ND	<2	<5	<15	<5	270	<50 ⁺
47,48,93.	<20 ⁺	<20	<5	<1	<1	<1	<1	<4	ND	<2	<5	<15	<5	100	<50 ⁺
89,90,101,105.	<5	<20	<5	<1	<1	<1	<1	<4	ND	<2	<15 ⁺	<15	<20 ⁺	30	<50 ⁺
<u>b) Sandy Sediments</u>															
24.	<10 ⁺	<10	<2	<0.5	<0.5	<0.5	<0.5	<1	<1	<0.5	11 ⁺	<10	<15 ⁺	<2	<25 ⁺
3	<10 ⁺	<10	<2	<0.5	1	<0.5	<0.5	<1	<1	<0.5	<2	<10	<3	6	<25 ⁺
49.	<2	<10	<2	<0.5	<0.5	<0.5	<0.5	<1	ND	<0.5	<10 ⁺	<10	<15 ⁺	6	<25 ⁺
52.	<2	<10	<2	<0.5	<0.5	<0.5	<0.5	<1	ND	<0.5	<10 ⁺	<10	<15 ⁺	<2	<25 ⁺
38 ¹	<2	<10	<2	1.5	0.7	<0.5	<0.5	<1	<1	<0.5	<10 ⁺	<10	<3	3	<5
54 ¹	<2	<10	<2	<0.5	<0.5	<0.5	<0.5	<1	ND	<0.5	<2	<10	<3	4	<5
55 ¹	<2	<10	<2	<0.5	<0.5	<0.5	<0.5	<1	ND	<0.5	<2	<10	<3	2	<5

1 Extracts not saponified

+ full scan data, otherwise SIR data

* for DDT full scan data refers to degradation product (DDMU)

N.D. - not determined

Note:- Figures prefixed by < denote lower detection limits for the sample type and analytical method (full scan or SIR)

Table 2. Target compounds unstable to isolation procedure

Environmental Sample	Lindane	Endosulphan	Organophosphorus compounds		
			Fenitrothion	Malathion	Parathion
<u>Sand sediments</u>					
38 ¹	<10	<15	<15	<10	<10
54 ¹	<10	<15	<15	<10	<10
55 ¹	<10	<15	<15	<10	<10
49	-	-	<50	<100	<50
52	-	-	<50	<100	<50
<u>Soil</u>					
89, 90, 101, 105	-	-	<100	<200	<100

1- Organic extract not saponified. For remaining samples in table, lindane + endosulphan not measurable; organophosphorus compounds each give a hydrolysis product having a higher detection limit than the parent compound. There were no detectable concentrations of the hydrolysis product in any of the other samples listed in Table 1.

Table 3. Additional data from full scan mass spectra.

Environmental Sample No ⁺	Abundance ng/g		Unusual features from full scan spectra [#]
	Fluoranthene	Naphthalenes*	
(a) Soils/Organic			
<u>Sediments</u>			
74,75,76	1180	670	$\alpha\beta$ -hopanes dominant
6,7,8	1400	800	
107	1500	200	
97,100,118	3000	30	
88,99,103	800	200	Taraxerone, friedelin abundant.
73	200	ND	Unidentified alkene/cycloalkane abundant
58	700	40	
59	130	150	
60	20	20	
32,35	2700	3000	$\alpha\beta$ -Hopanes dominant n-Alkanes in range C ₁₃ -C ₂₇ show very low $\frac{\text{odd}}{\text{even}}$ ratio
96	5100	1300	$\alpha\beta$ -Hopanes dominant
47,48,93	2500	140	
89,90,101,105(a)	800	40	Natural hopanes dominant
(b) Sandy Sediments			
24	<20	N.D.	
3	100	20	
49(a)	160	20	A natural hopane is dominant.
52(a)	<20	N.D.	$\alpha\beta$ hopanes dominant. n-Alkanes below C ₂₇ show low $\frac{\text{odd}}{\text{even}}$ ratio
38(b)	90	N.D.	$\alpha\beta$ -Hopanes dominant.
54(b)	30	40	$\alpha\beta$ -Hopanes dominant n-Alkanes (C ₂₂ -C ₂₈) show low $\frac{\text{odd}}{\text{even}}$ ratio
55(b)	40	N.D.	$\alpha\beta$ -Hopanes dominant.

+ (a) Neutral and acidic components separated after hydrolysis (b) Extract not hydrolysed
* ND - not detectable.

- # Notes:- 1. Dominance of $\alpha\beta$ -hopanes (over natural $\beta\beta$ -hopanes) and the 1:1 ratio of S and R isomers at C₃₁ is indicative of pollution from thermally mature geolipids, usually petroleum products. High fatty acid concentration in the extracts often obscured this data, hence it is only given for sediments extracted under modified conditions (a) or (b), except for 74/75/76 sample where a duplicate extraction was performed and samples 32/35 and 96, which are also highly polluted by aromatic hydrocarbons.
2. Low odd/even ratio of n-alkanes also suggestive of petroleum pollution or dominance of bacterial input.
3. Identification of taraxerone + friedelin in sample 88/99/103. This sample gave the largest lipid extract, three times as much as any other soil. Taraxerone and friedelin are higher-plant products, occurring in both tree and grass species.

Fig. 1. Total ion chromatograms of soils having high (top) and low (bottom) abundances of PAH and alkyl naphthalenes.

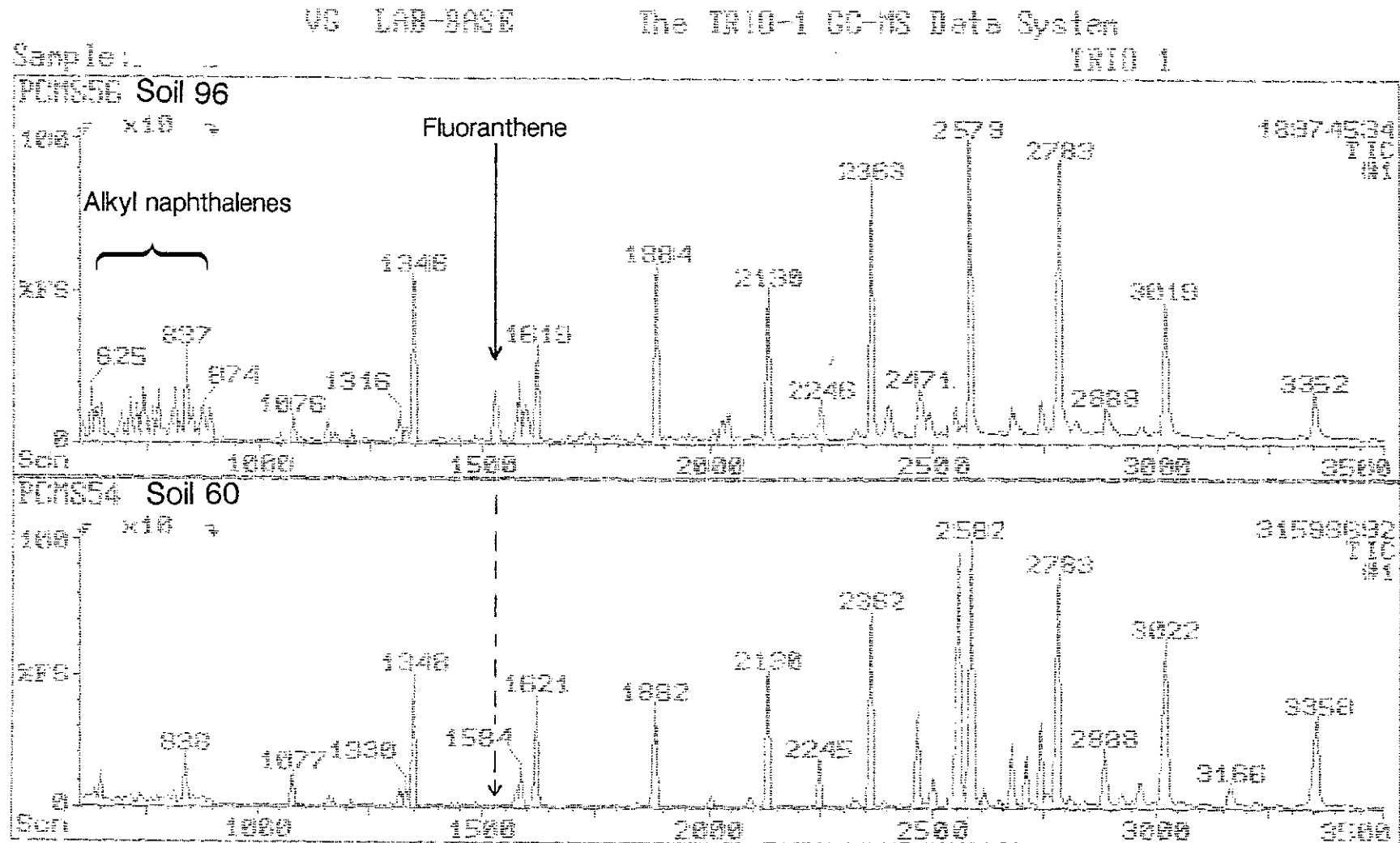


Fig. 2. Total ion chromatograms of soil showing highest lipid content but low in pollutants (upper) and soil showing highest alkyl naphthalenes (lower)

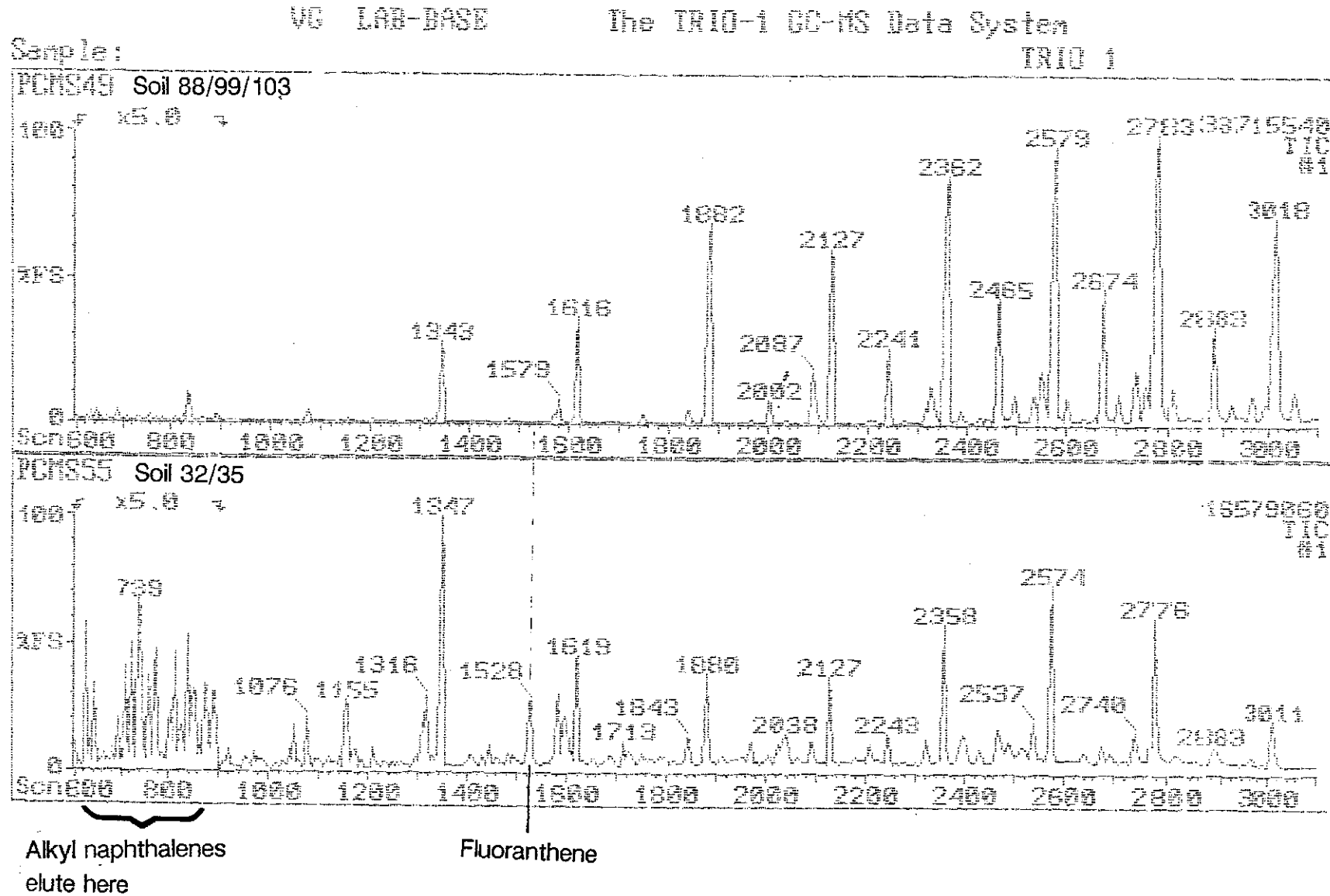


Fig.3. Total ion chromatograms showing neutral lipid distributions typical of a soil (upper) and a sandy sediment (lower).

VG LAB-BASE

The TMS-1 GC-MS Data System

Sample:

