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APPENDICES

Appendix A: Chromatography (High Performance Thin Layer (HPTLC), Gas Chromatography Mass Spectrometry (GCMS) and High Performance Liquid Chromatography (HPLC)). Kovats Analysis and Fourier Transform Infrared Spectrometry (FTIR).

Appendix B: Size Fractionation of Dried Soils of the Yorke Peninsula.

Appendix A

High performance thin layer chromatography (HPTLC)

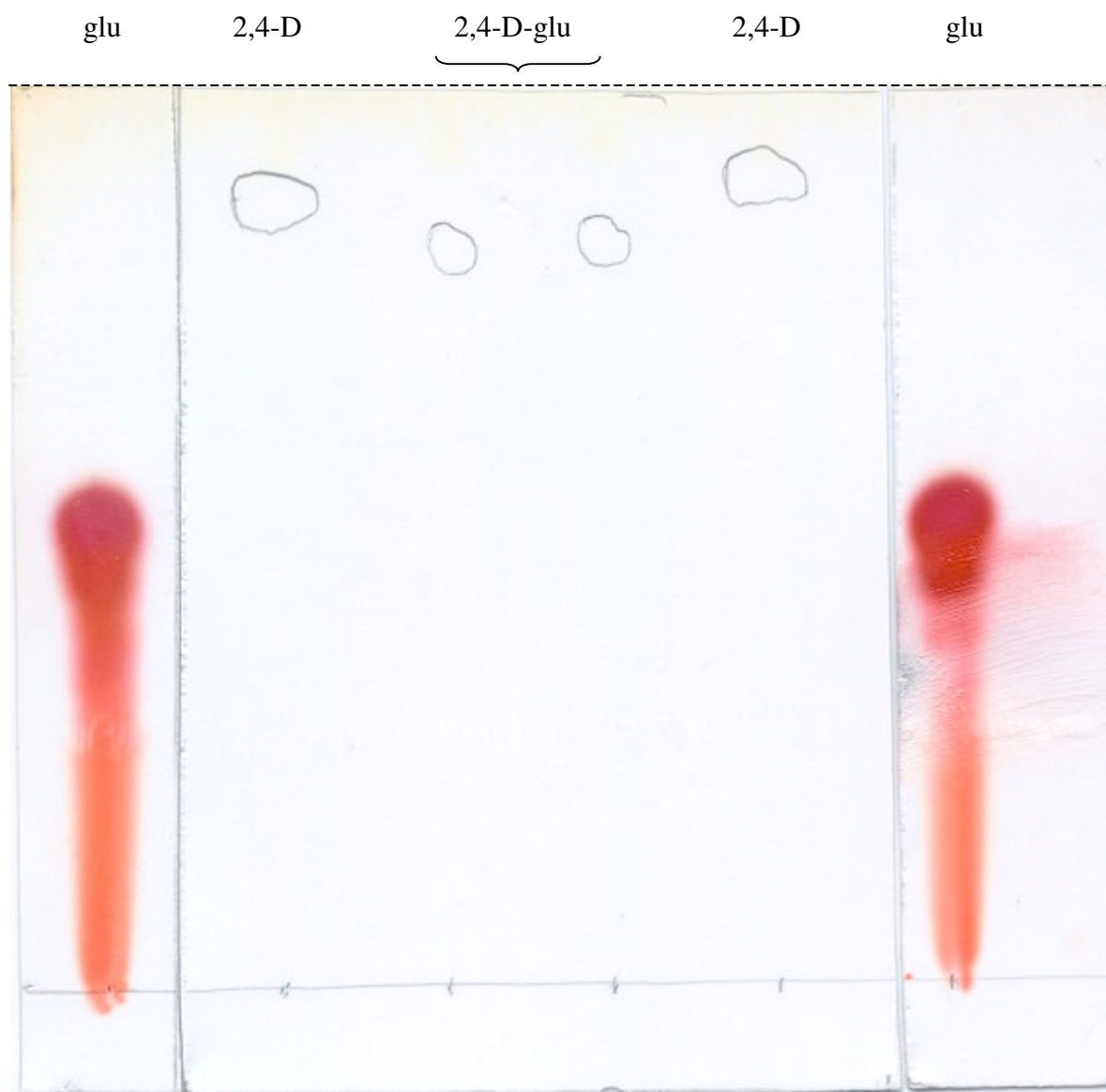


Figure A1: High performance thin layer chromatography of glutamic acid (glu), 2,4-dichlorophenoxyacetic acid (2,4-D) and the conjugate of 2,4-D and glu (2,4-D-glu). The dashed line represents the solvent front.

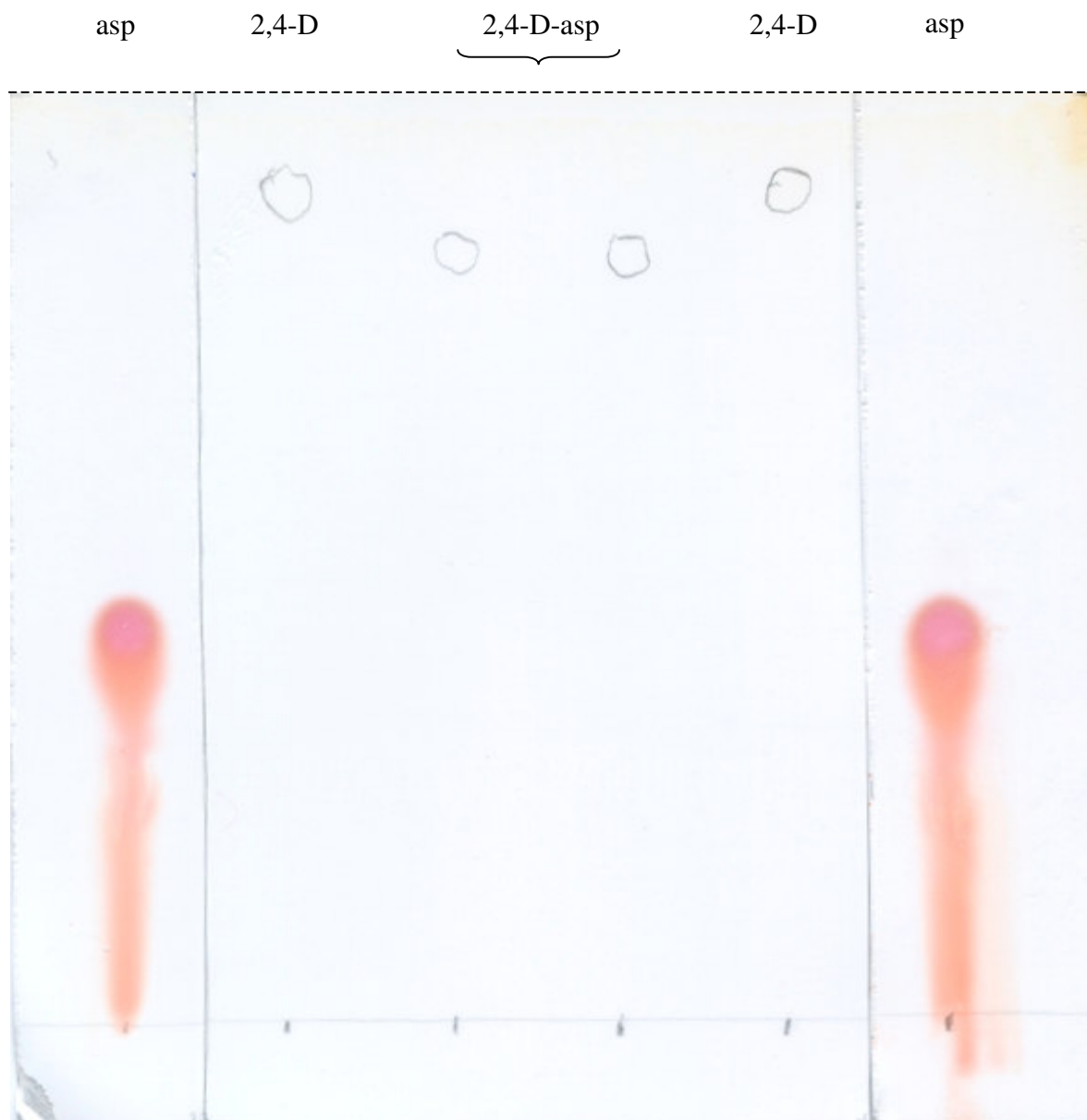


Figure A2: High performance thin layer chromatography of aspartic acid (asp), 2,4-dichlorophenoxyacetic acid (2,4-D) and the conjugate of 2,4-D and asp (2,4-D-asp). The dashed line represents the solvent front.

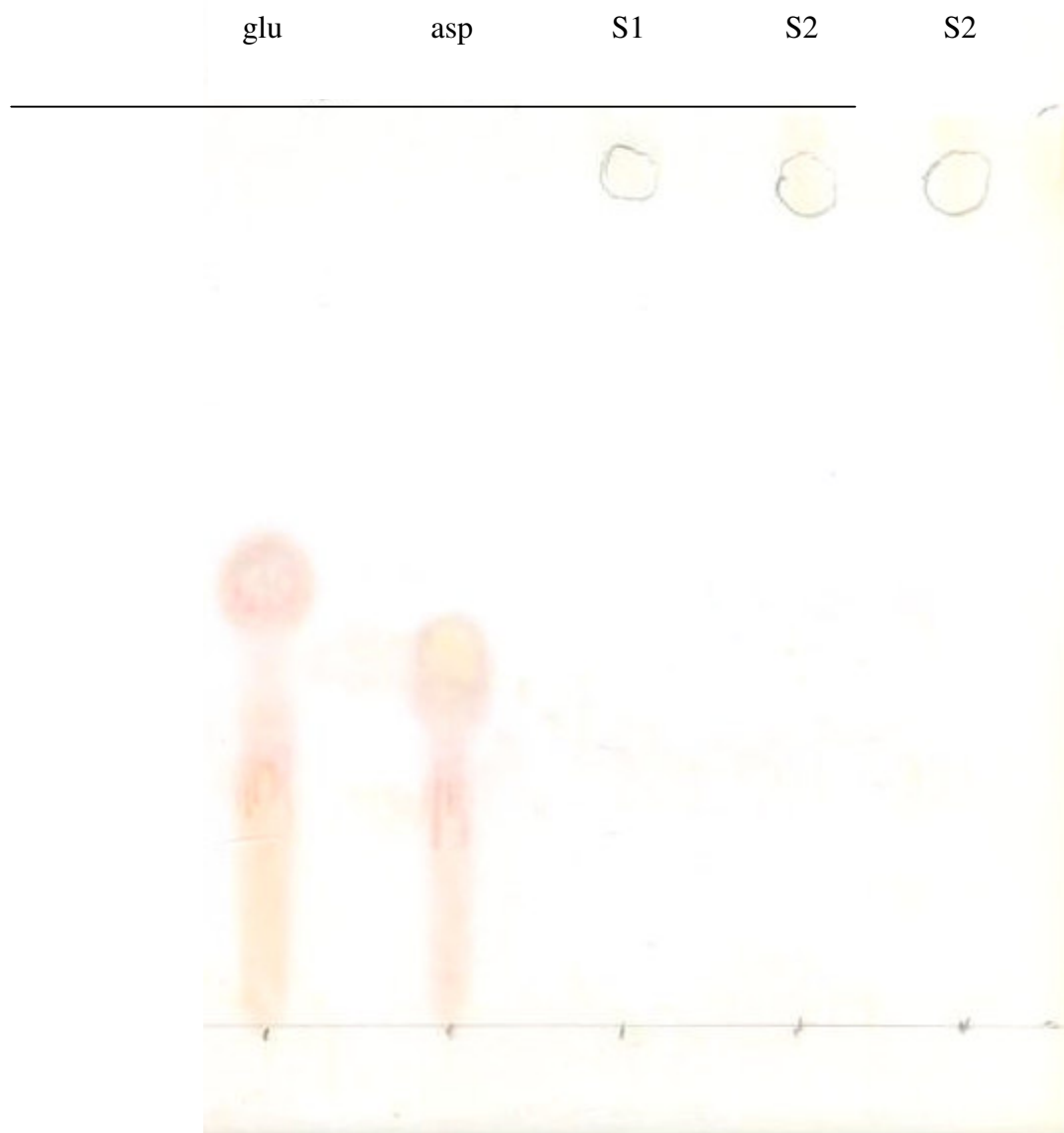
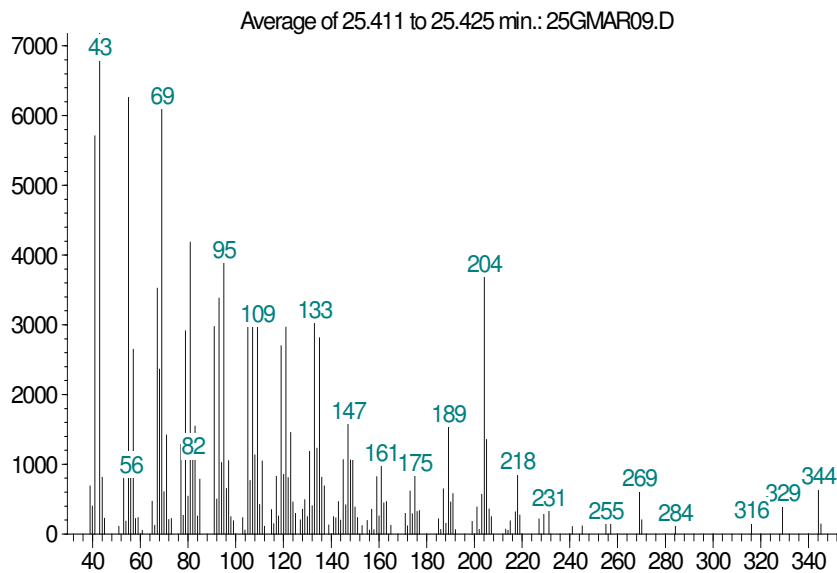


Figure A3: High performance thin layer chromatography of aspartic acid (asp), glutamic acid (glu) and three soil extracts (S1, S2 and S3). The dashed line represents the solvent front.

Abundance



m/z->

Figure A4 (a): Mass spectral profile of an analyte obtained from soil extracts that eluted at the solvent front in HPTLC preparations

Abundance

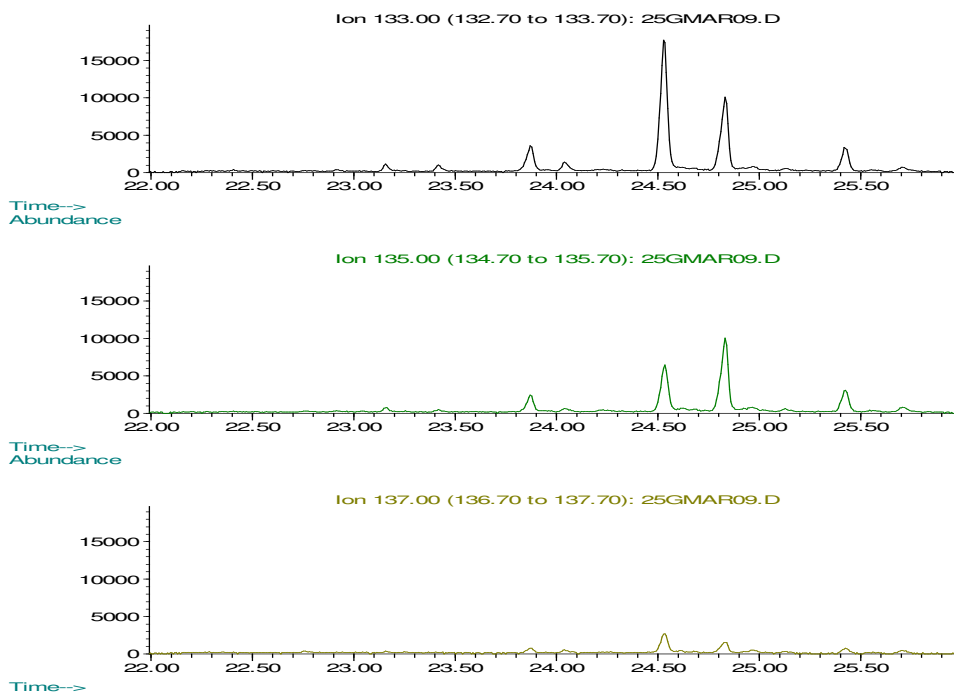


Figure A4 (b): Isotopic ratio analysis of analytes obtained from soil extracts that eluted at the solvent front in HPTLC preparations (m/z 133, 135 and 137).

Figure A4: Isotope ratio analysis of soil extracts

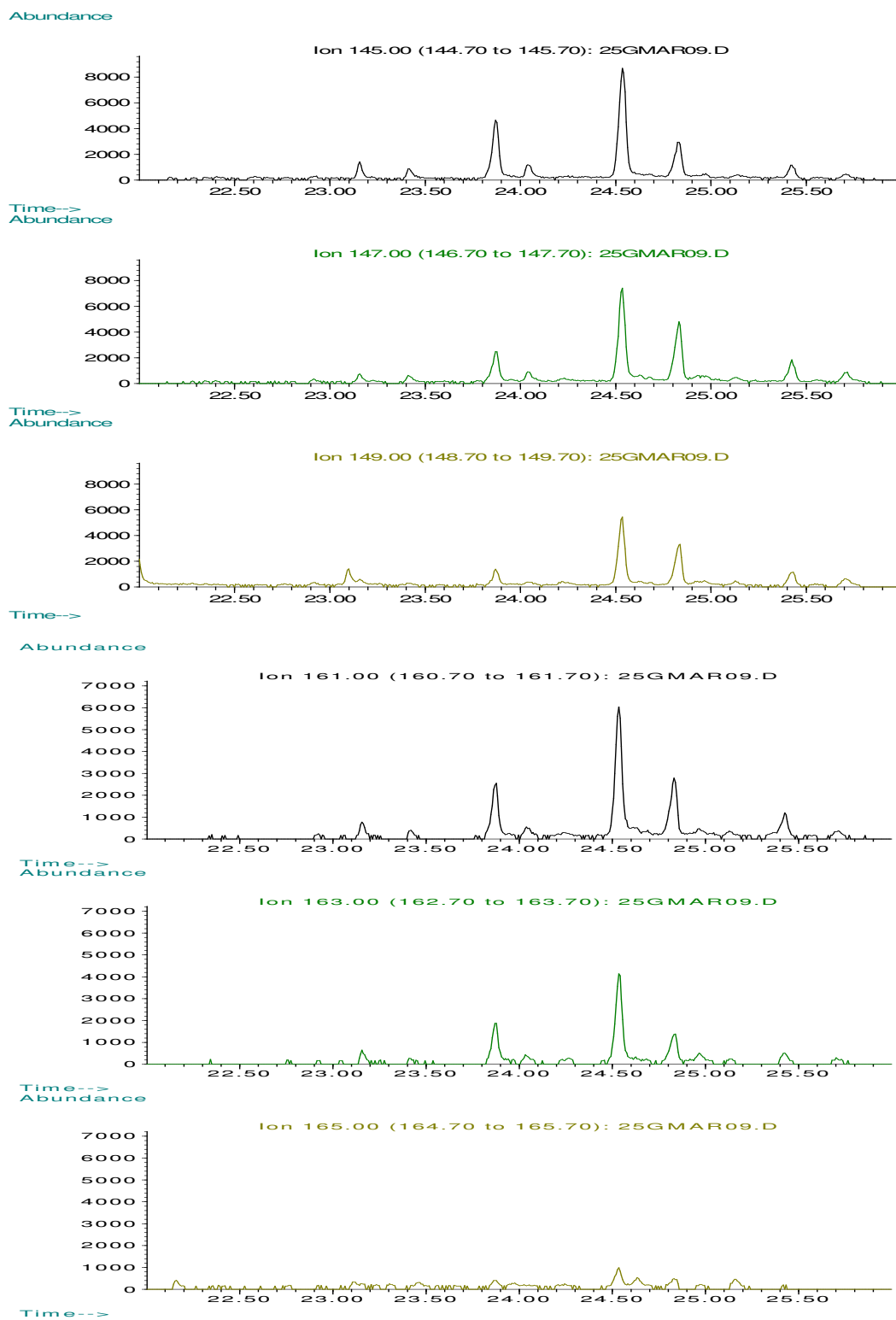
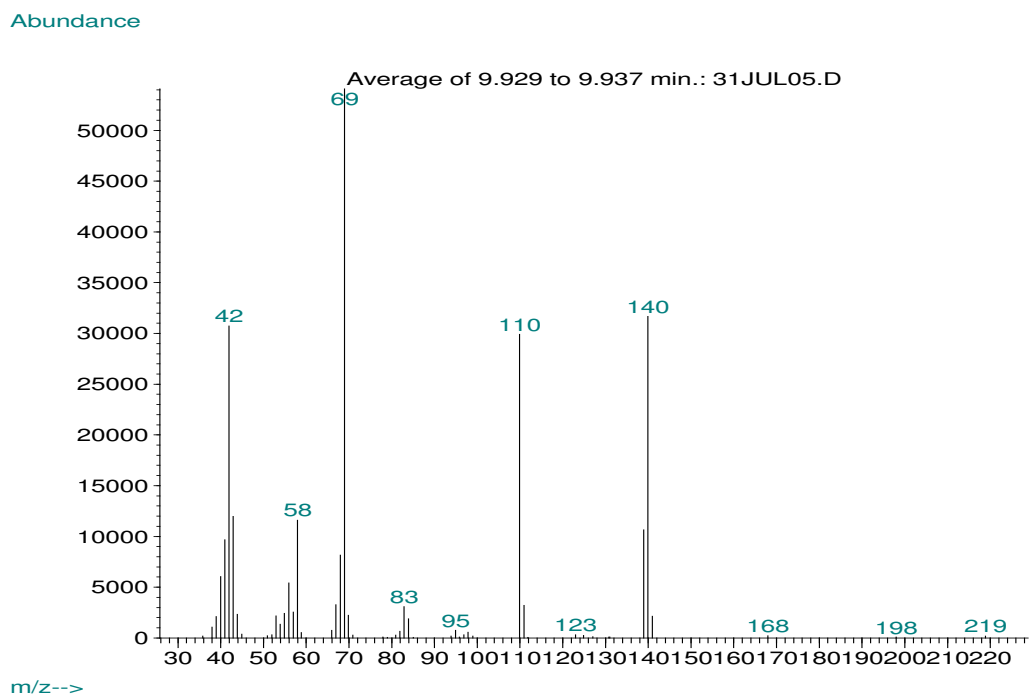


Figure A4 (b) continued: Isotopic ratio analysis of analytes obtained from soil extracts that eluted at the solvent front in HPTLC preparations (m/z 145, 147, 149 and 161, 163, 165).

(a)



(b)

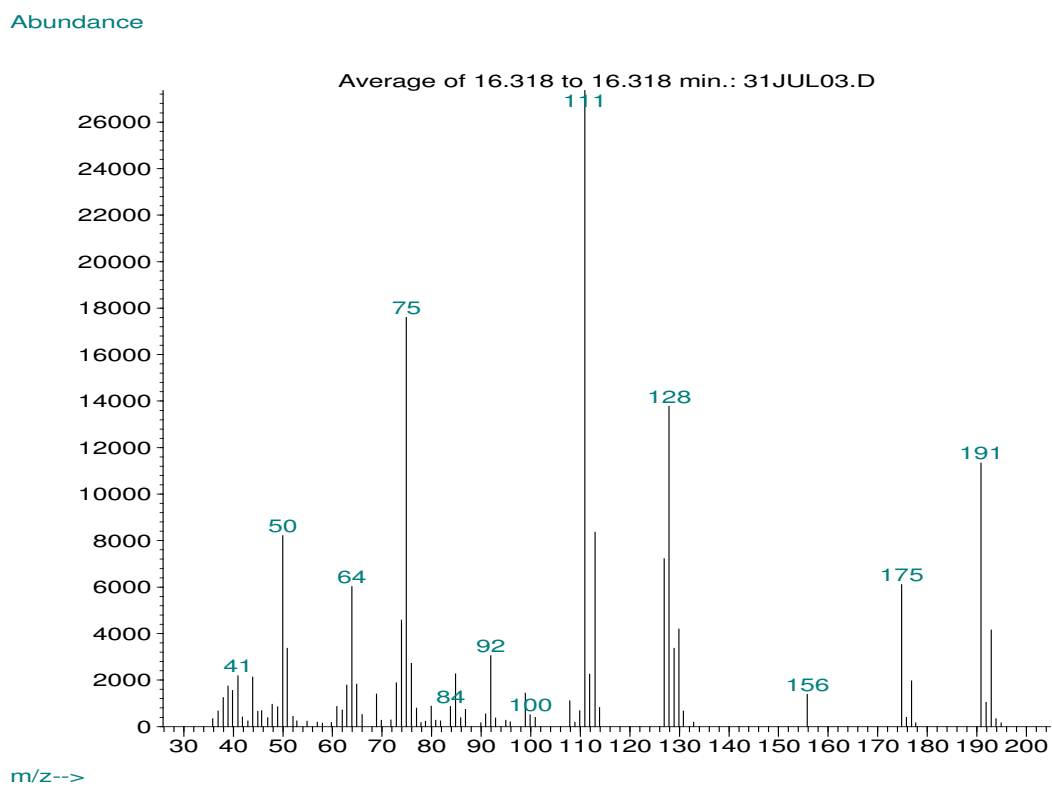


Figure A5: Pyrolysis products and mass spectra of the triazine moiety (a) and the non-triazine moiety (b) of chlorsulfuron (a sulfonyleurea herbicide).

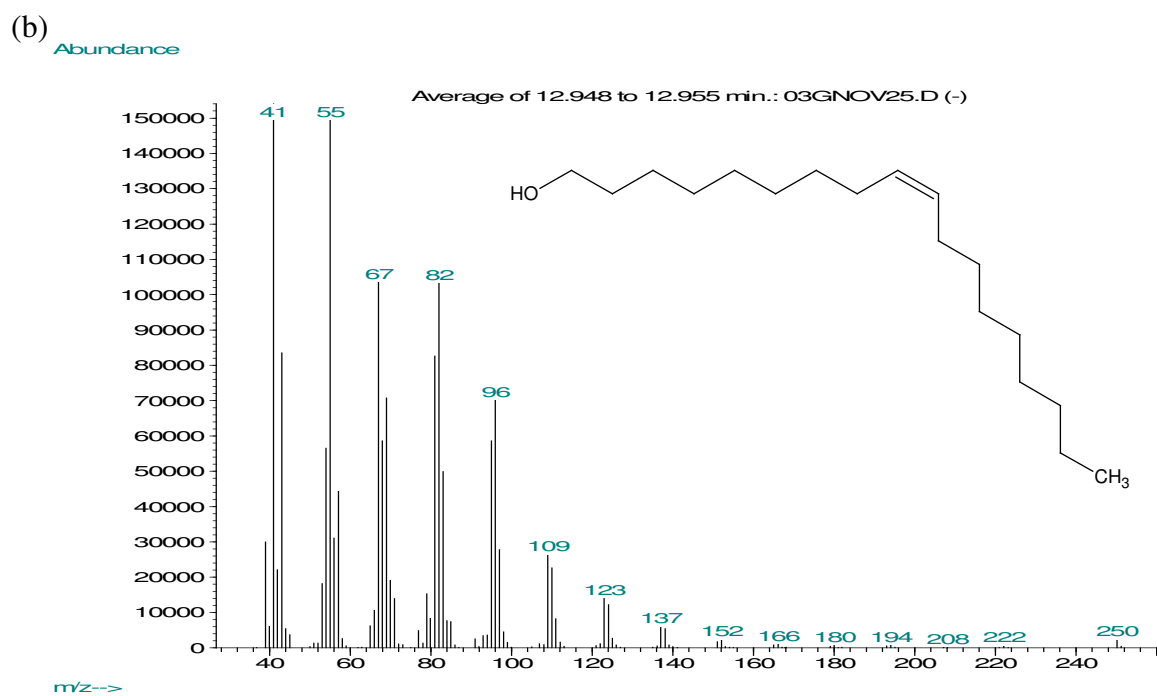
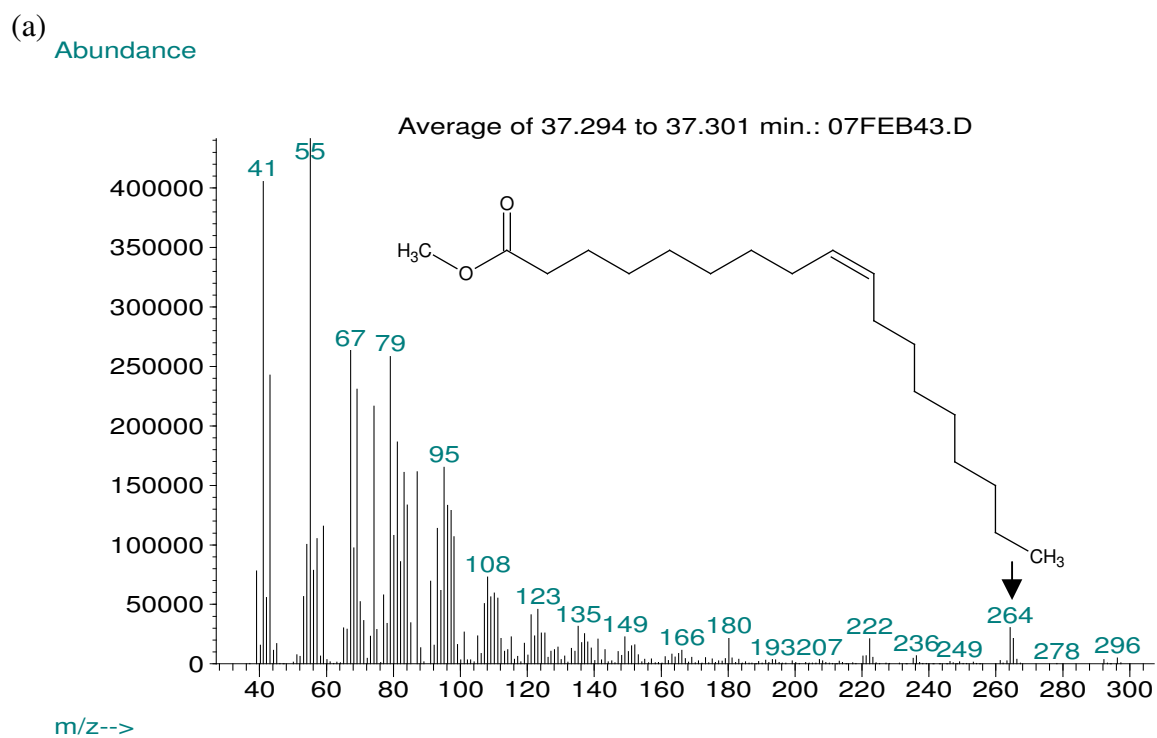


Figure A6: The mass spectra of 9-Octadecenoic acid methyl ester (a) and Oleoyl alcohol (b)

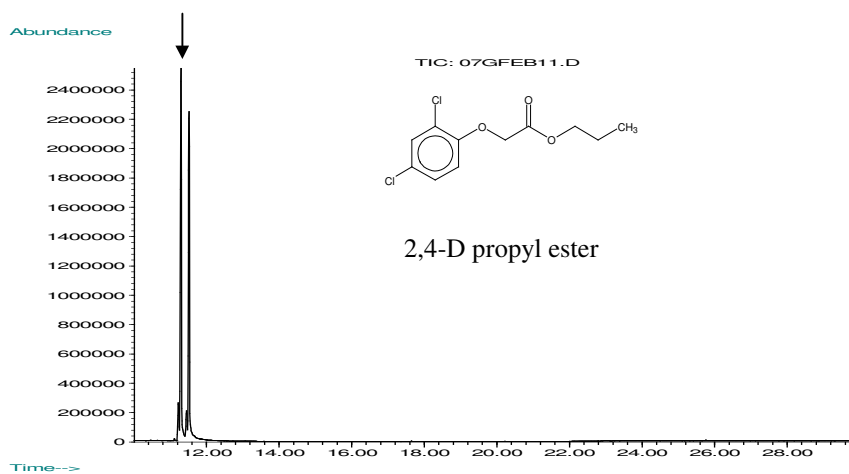
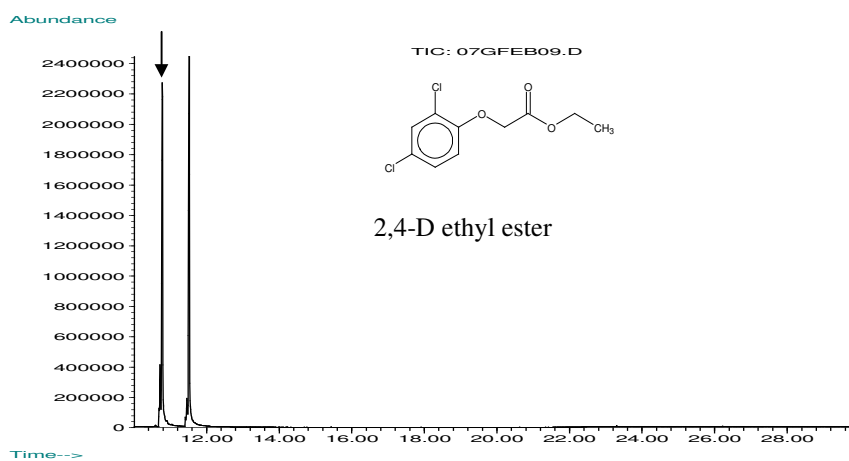
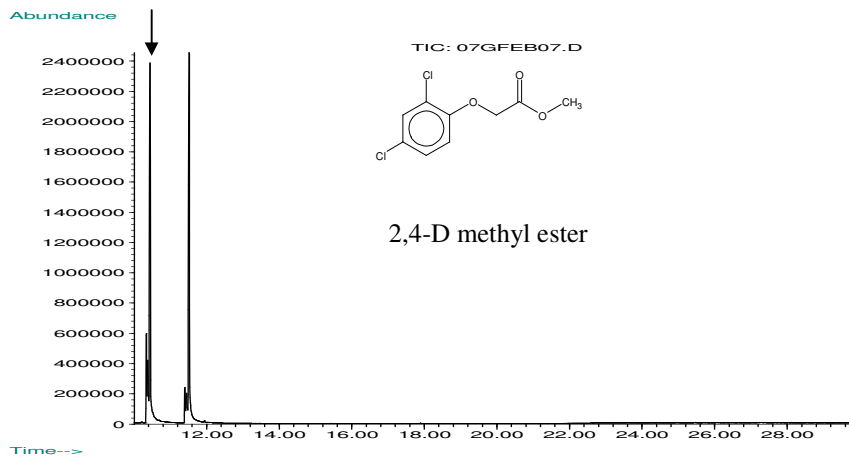


Figure A7: GCMS analysis of twelve aliphatic esters of 2,4-D.

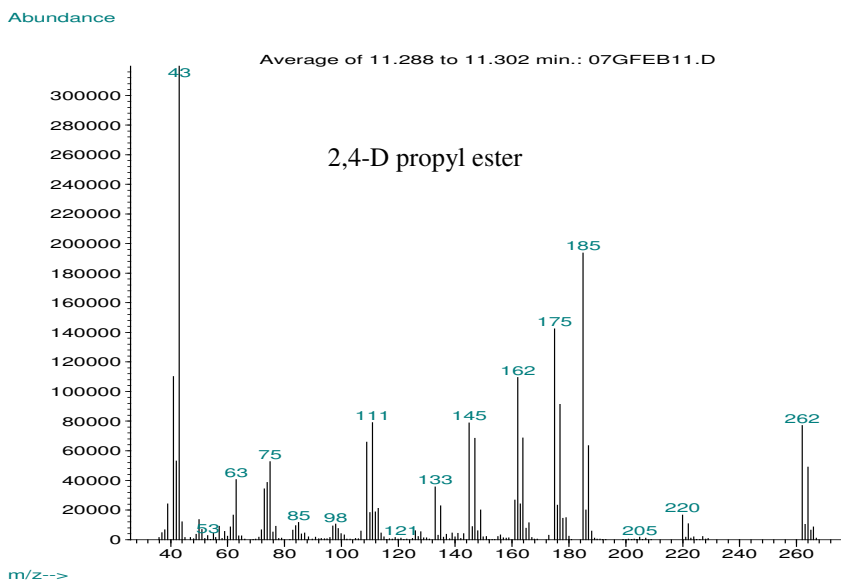
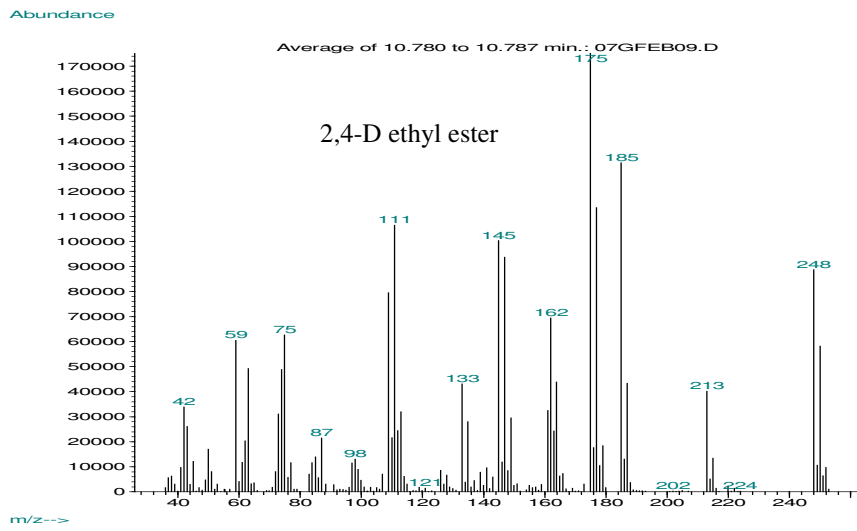
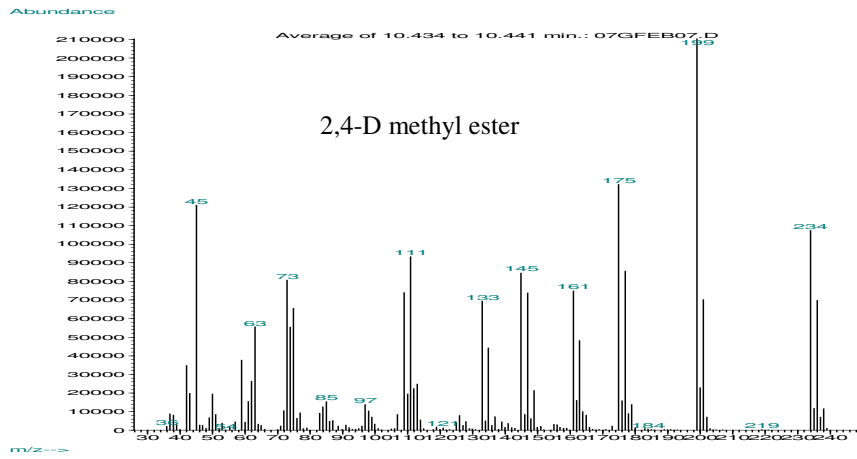


Figure A7: (continued).

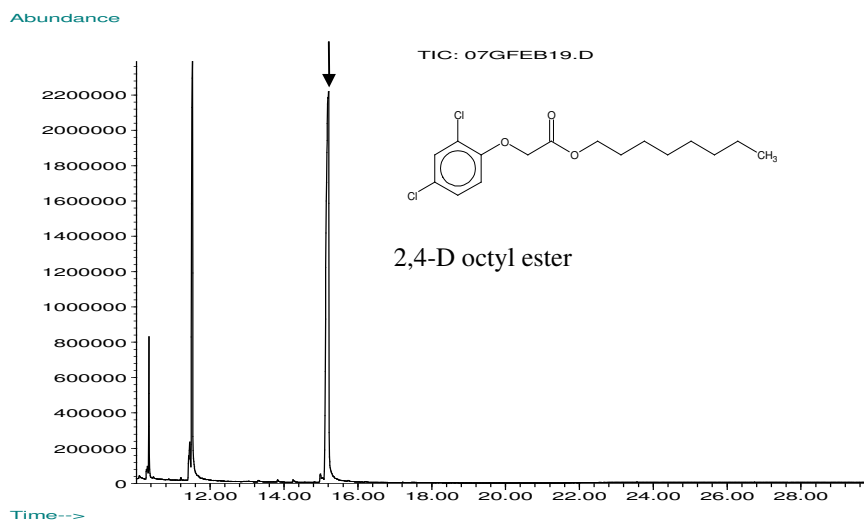
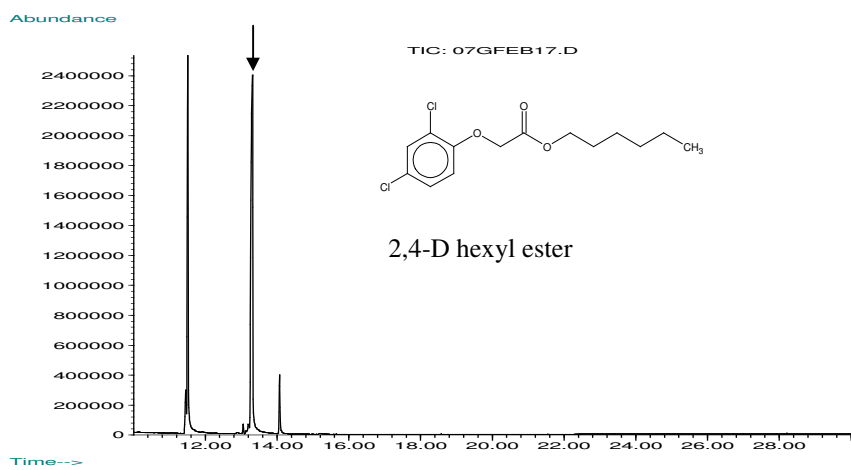
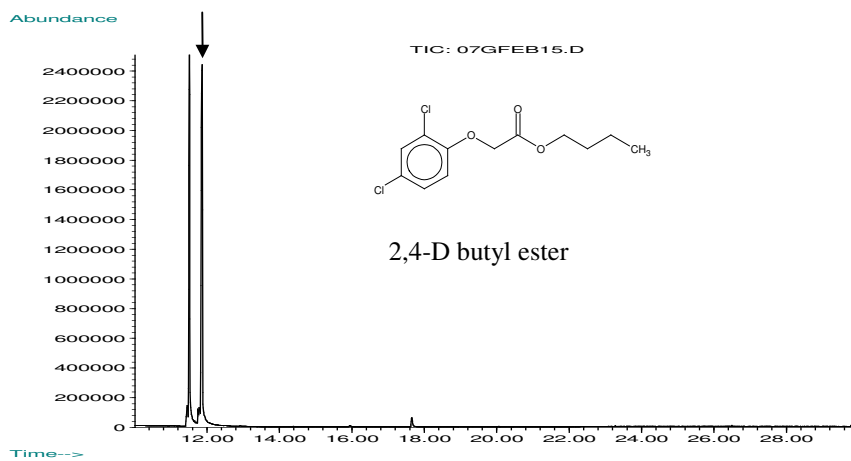
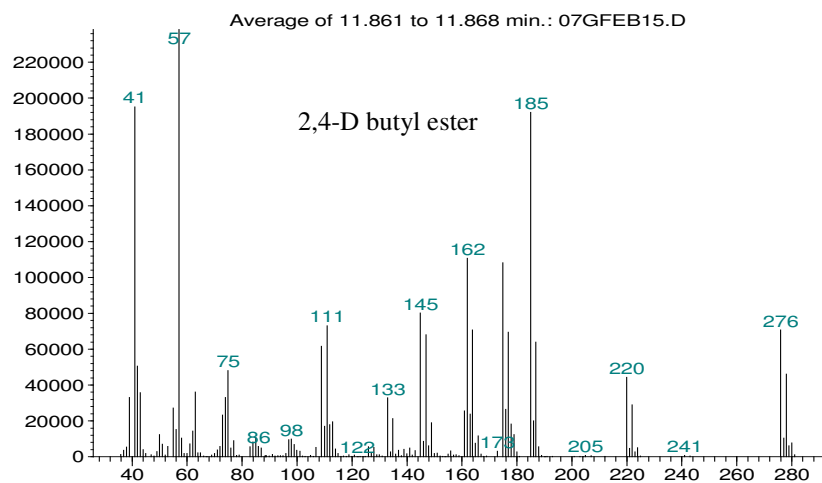


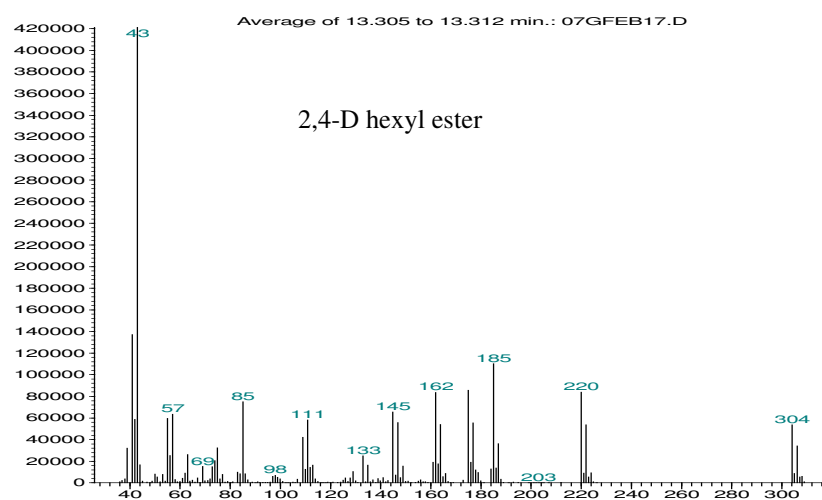
Figure A7: (continued).

Abundance



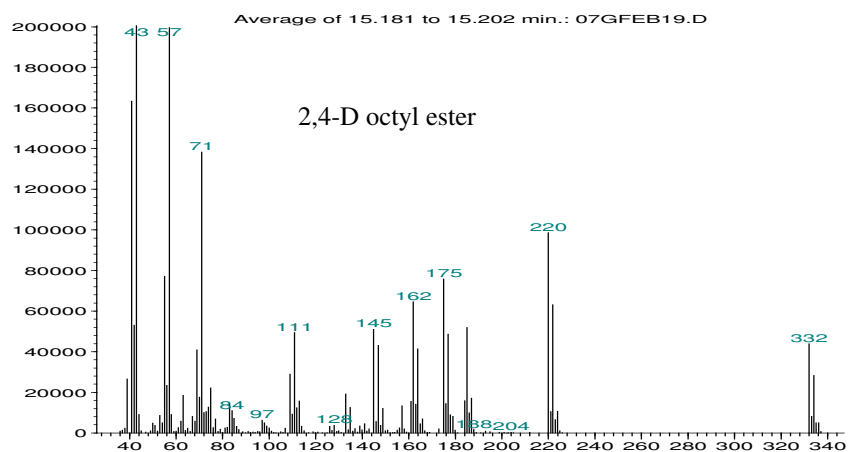
m/z-->

Abundance



m/z-->

Abundance



m/z-->

Figure A7: (continued).

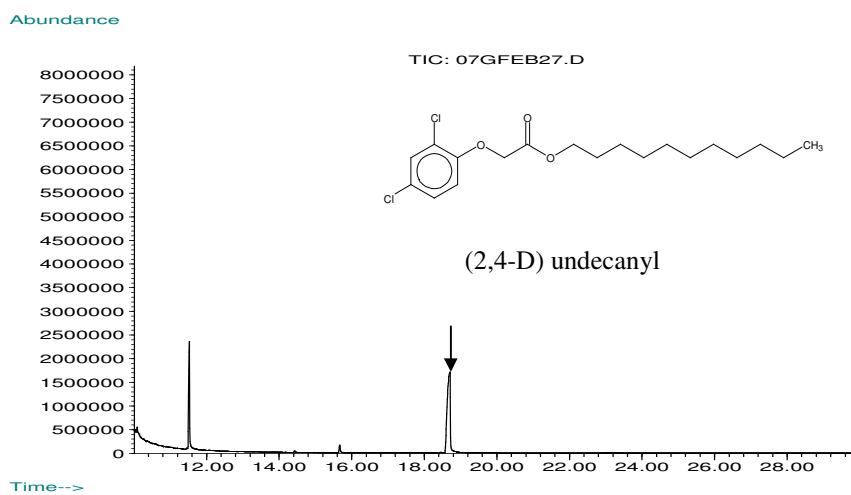
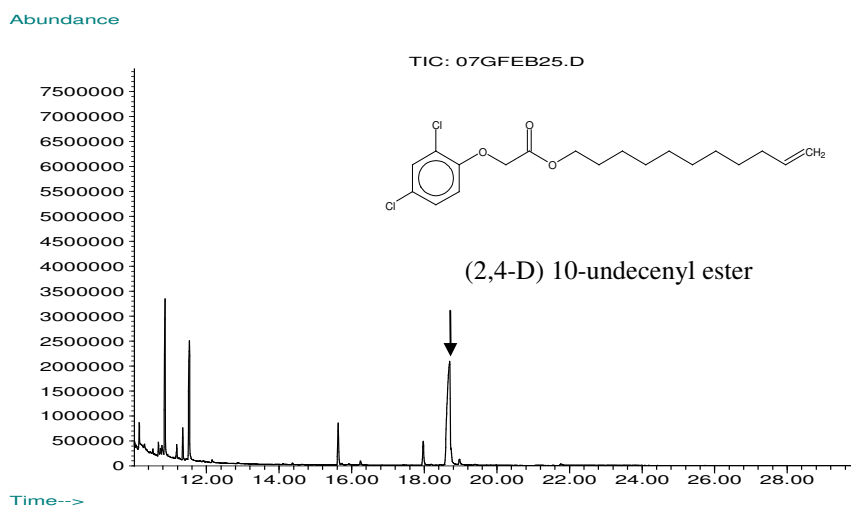
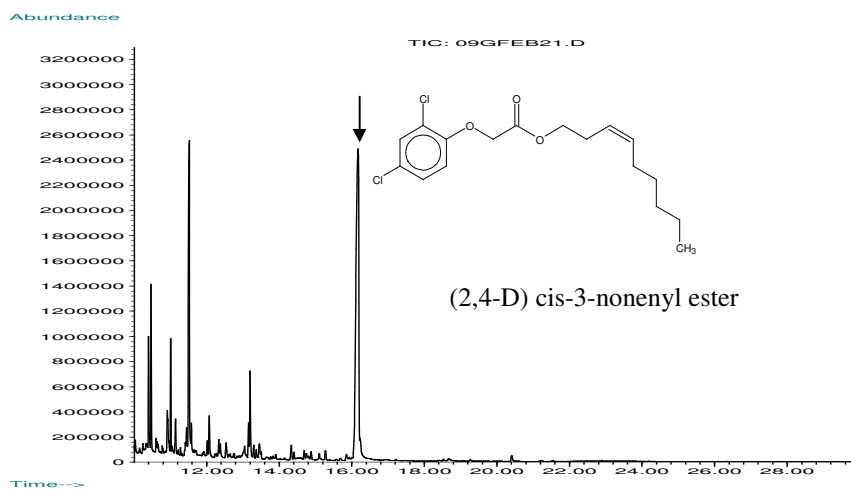


Figure A7: (continued).

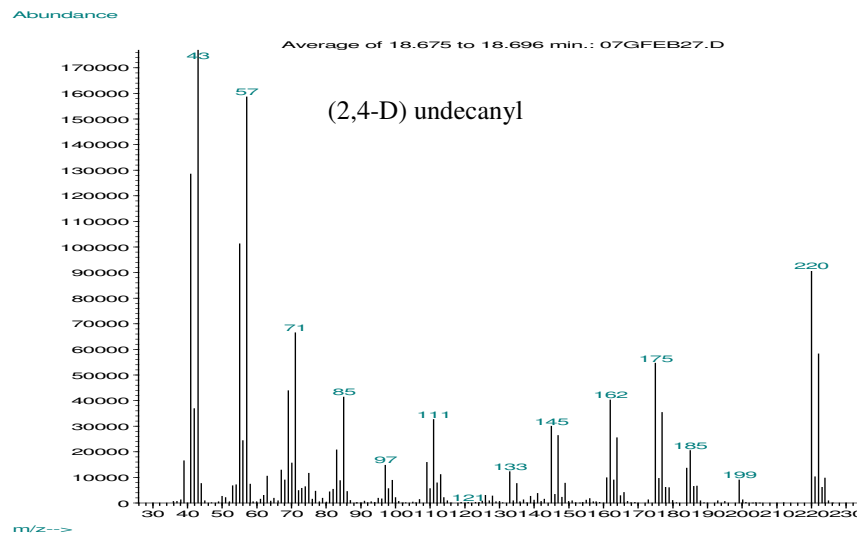
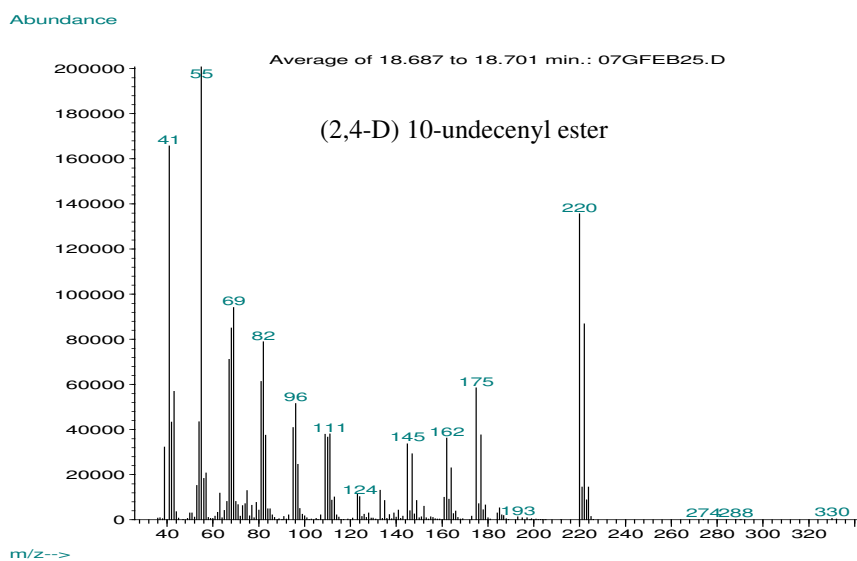
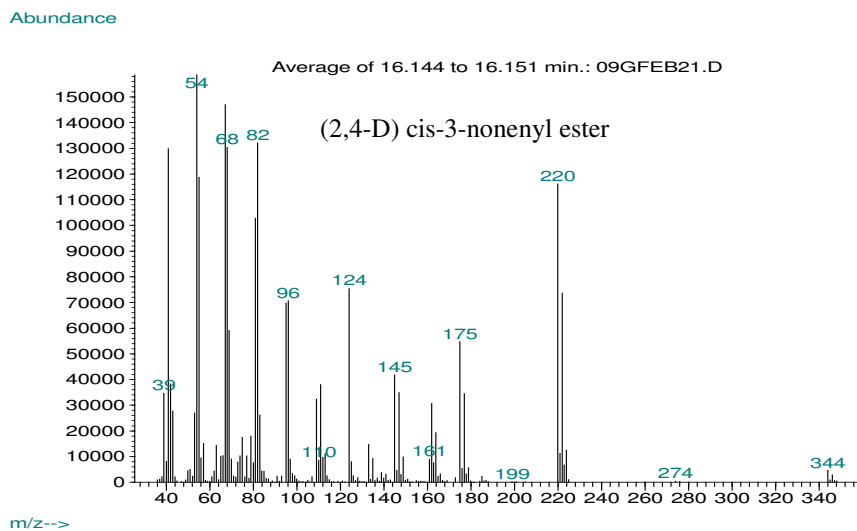


Figure A7: (continued).

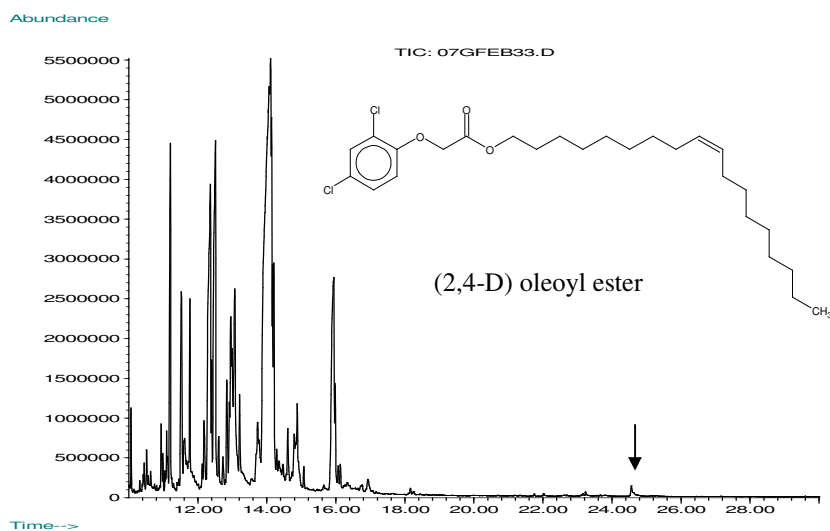
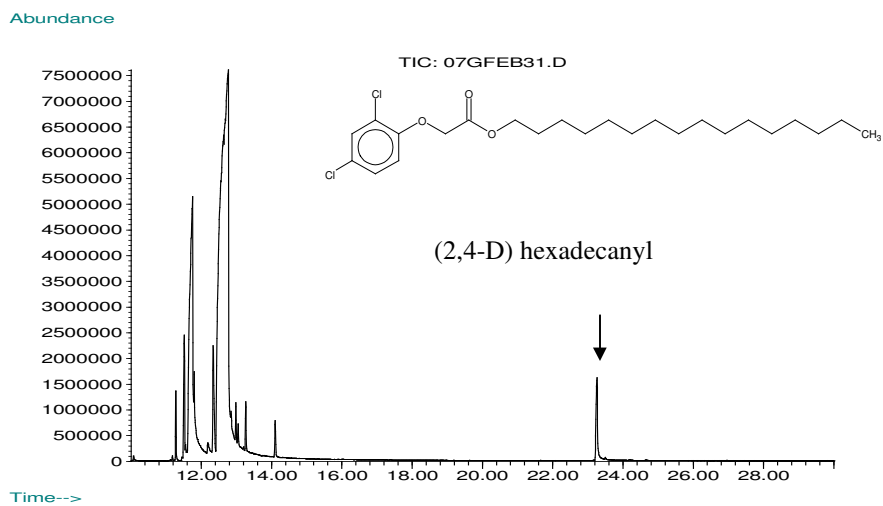
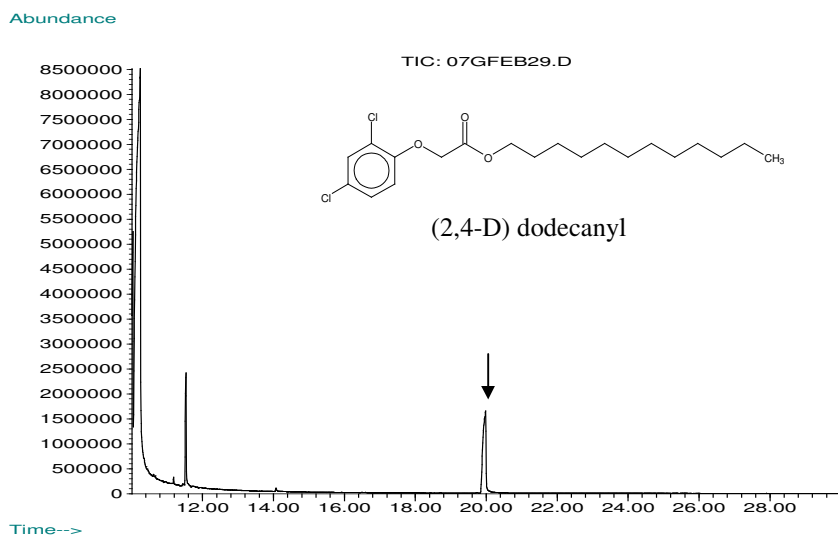


Figure A7: (continued).

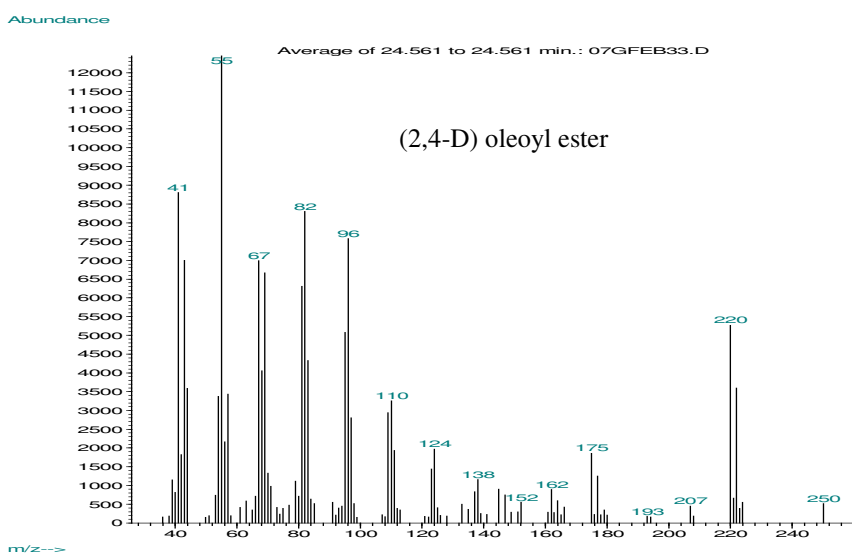
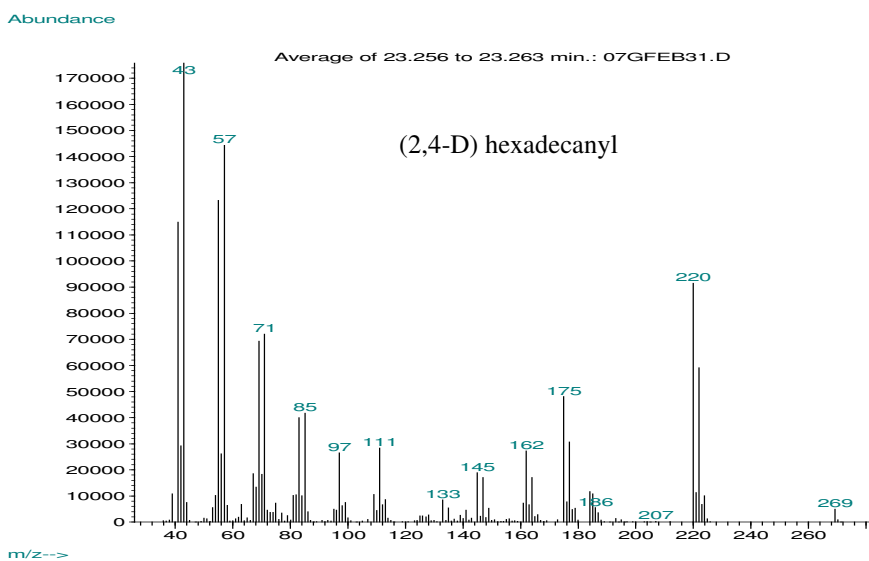
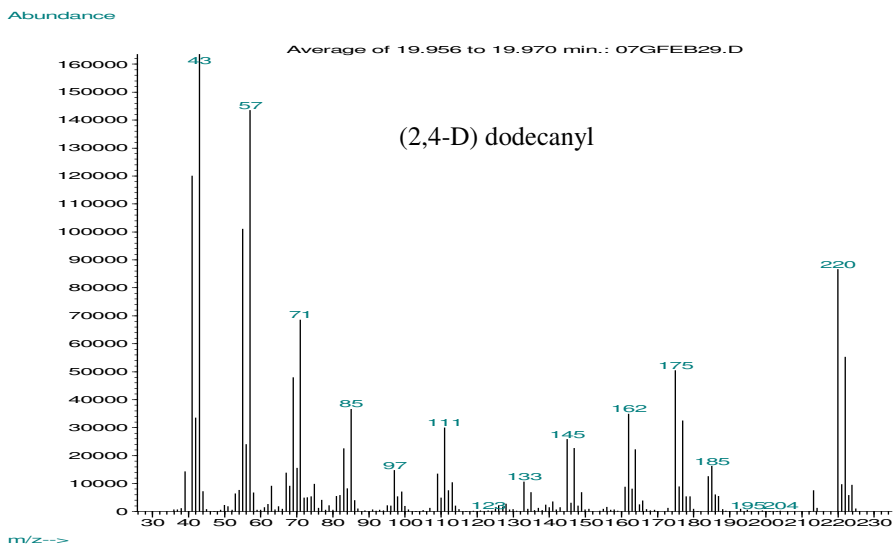


Figure A7: (continued).

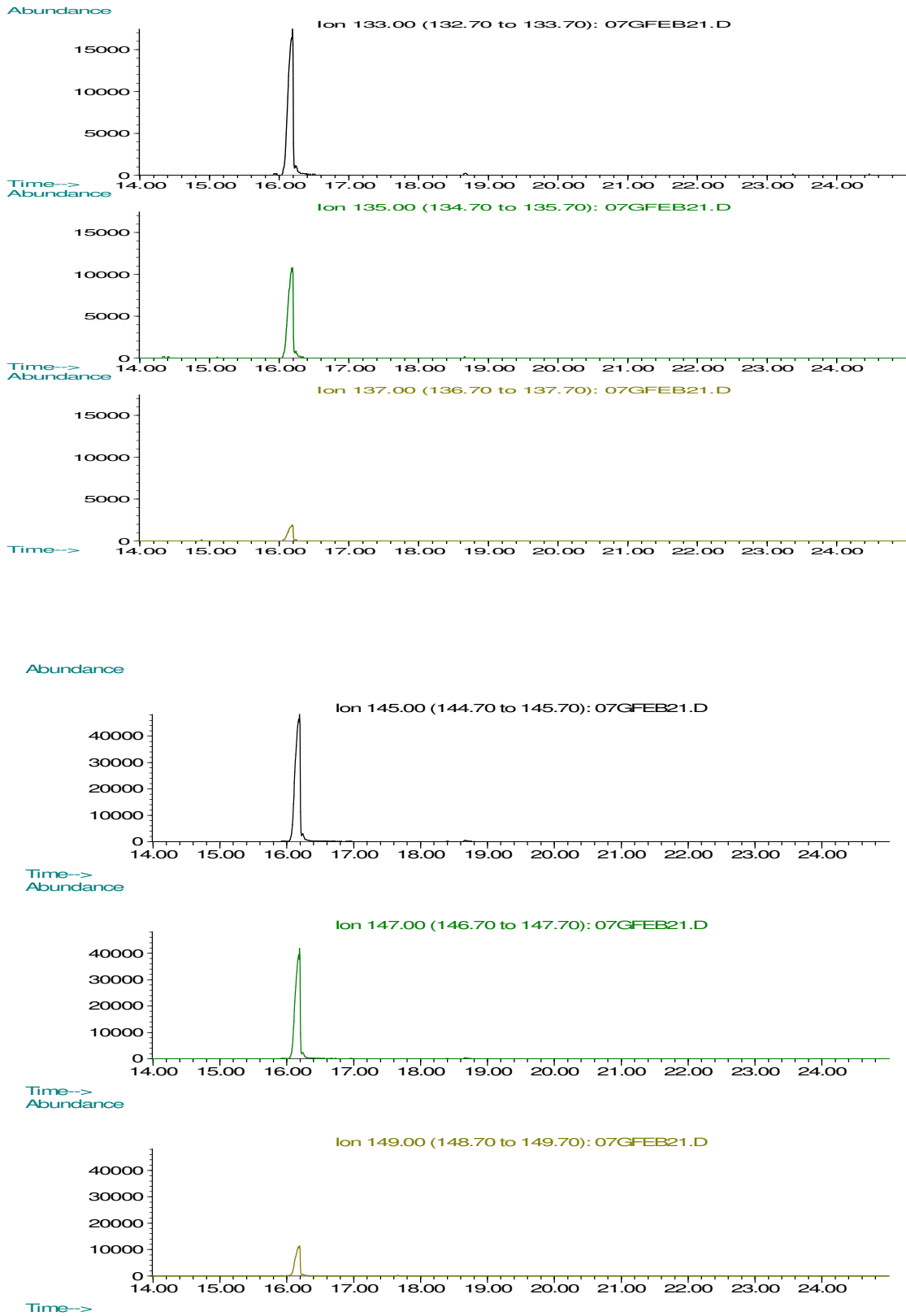
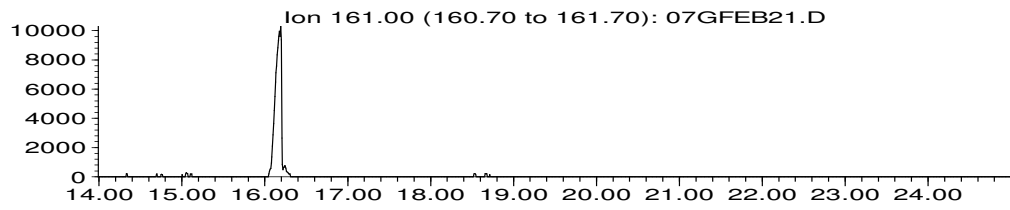
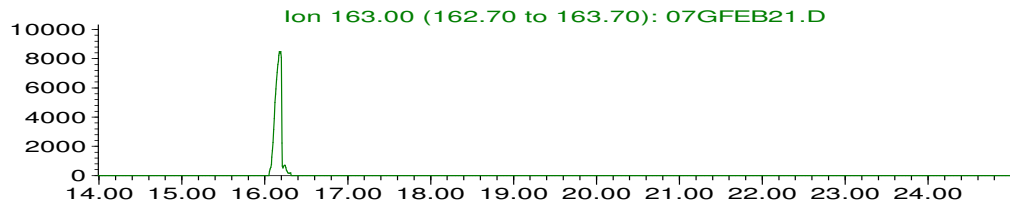


Figure A8: Isotope ratio analysis of the nonenyl ester of 2,4-D prepared by the method of Sanchez *et al.* (1991).

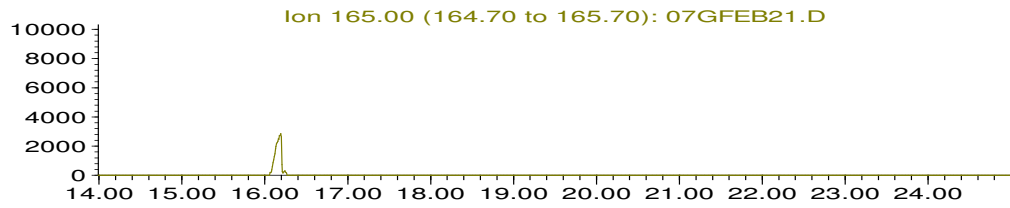
Abundance



Time-->
Abundance



Time-->
Abundance



Time-->

Figure A8: (continued).

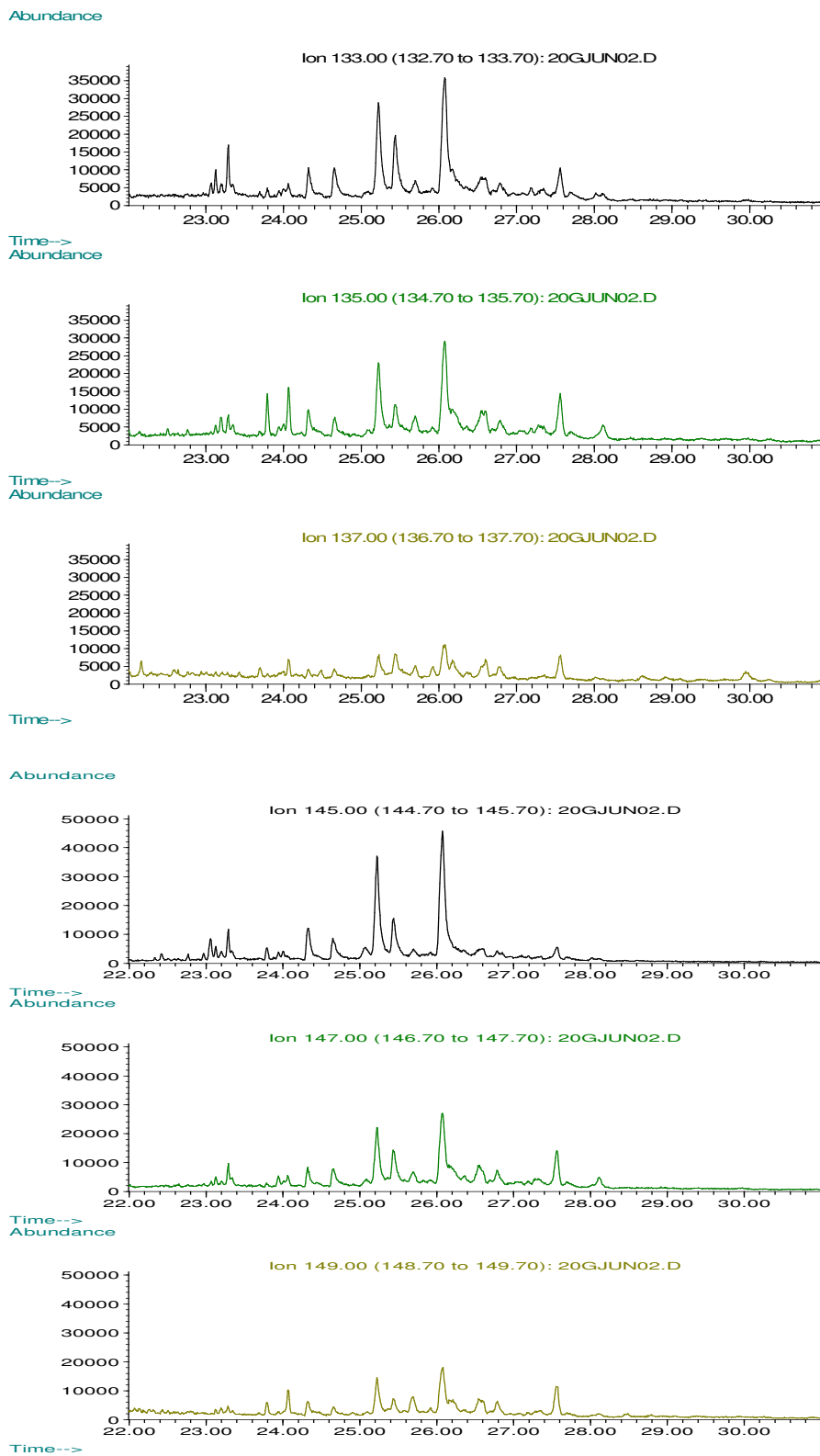


Figure A9: Isotope ratio analysis of whole soil #91

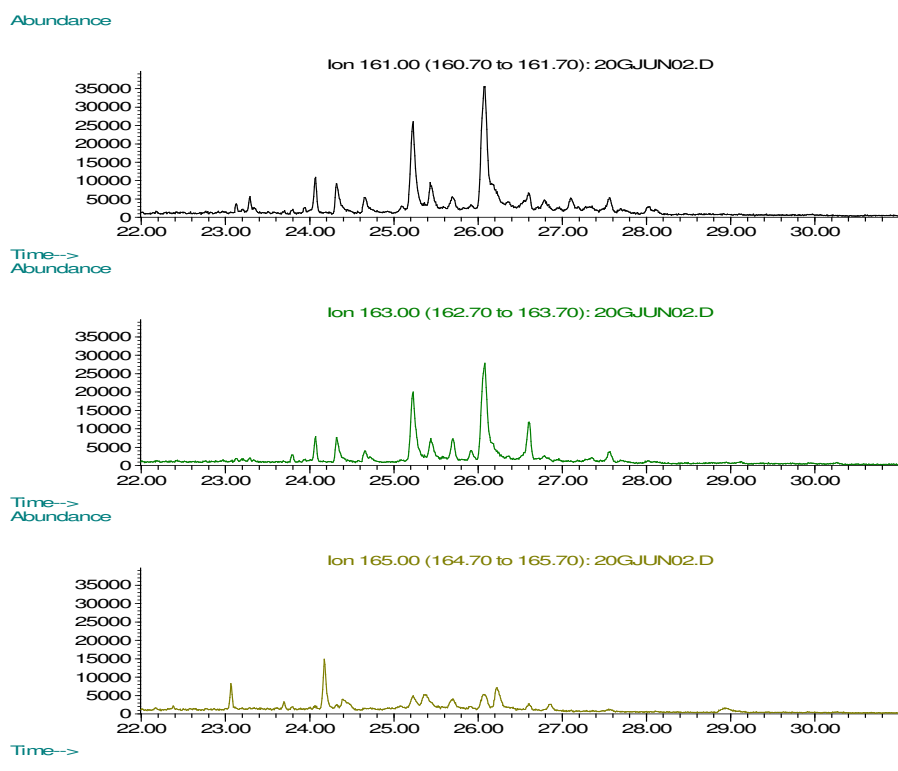


Figure A9: (continued).

Abundance

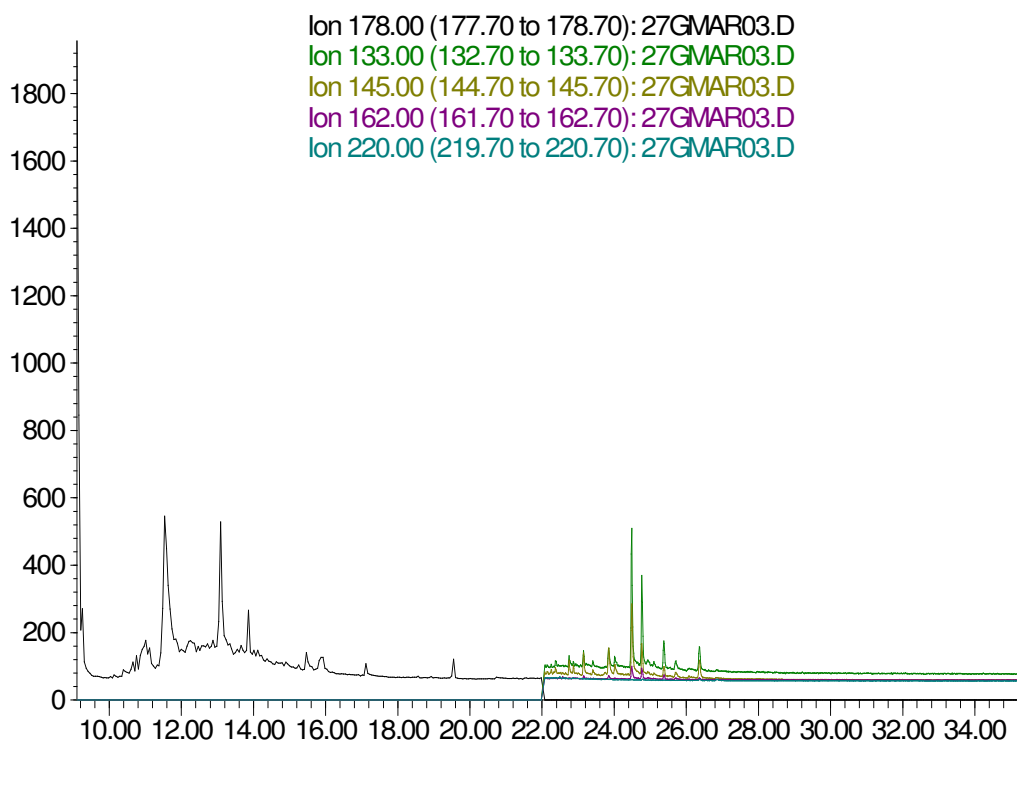
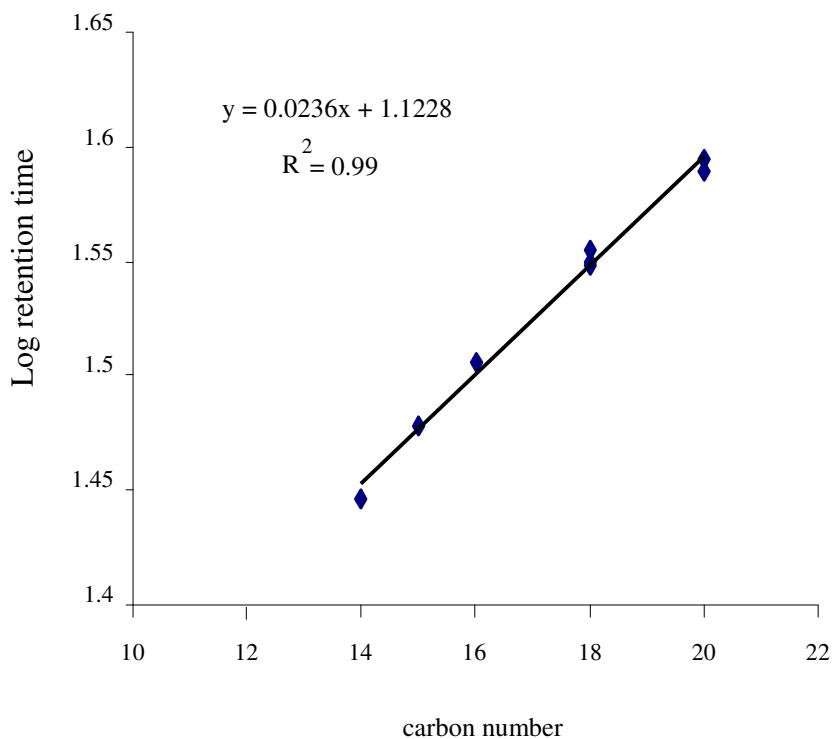


Figure A10: GCMS analysis of dust (fraction 5) obtained from soil #47

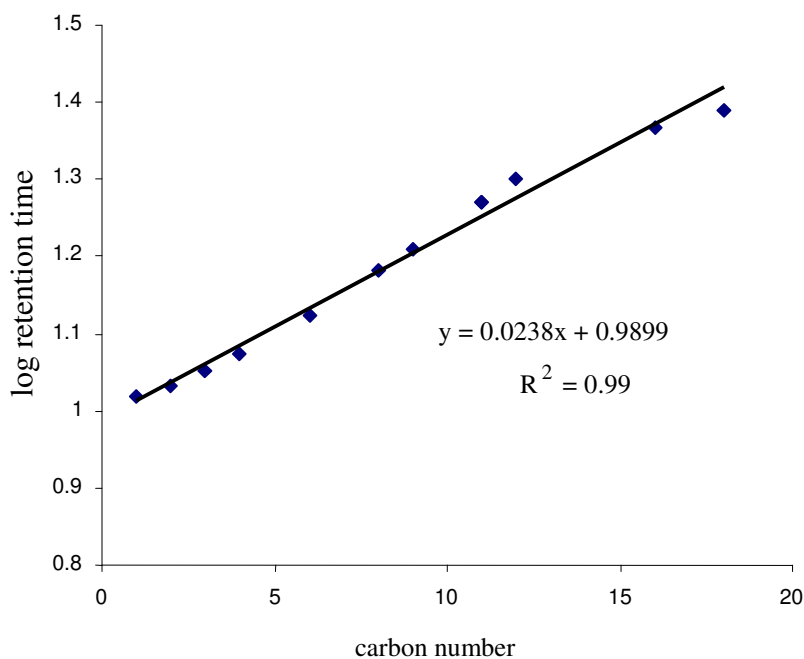
Note: $m/z = 220$ was not detected. A high quality control (HQC) mixture of herbicides and a dust 'blank', containing no herbicide, also showed no response other than for the internal standard emphasizing the specificity of the methodology for 2,4-D and 2,4-D like compounds.

Kovats analysis of fatty acid methyl esters



Eight fatty acid methyl esters were analysed: tetradecanoic acid methyl ester (14:0); pentadecanoic acid methyl ester (15:0); hexadecanoic acid methyl ester (16:0); 9,12 octadecadienoic acid methyl ester (18:2); 9 octadecenoic acid methyl ester (18:1); octadecanoic acid methyl ester (18:0); 11-eicosenoic acid methyl ester (20:1); eicosanoic acid methyl ester (20:0).

Kovats analysis of 2,4-D aliphatic esters



Twelve aliphatic esters of 2,4-D were analysed: 2,4-D methyl ester; 2,4-D ethyl ester; 2,4-D propyl ester; 2,4-D butyl ester; 2,4-D hexyl ester; 2,4-D octyl ester; (2,4-D) cis-3-nonenyl ester; (2,4-D) 10-undecenyl ester; (2,4-D) undecanyl; (2,4-D) dodecanyl; (2,4-D) hexadecanyl and (2,4-D) oleoyl ester.

Figure A11: Kovats analysis of retention time data.

Kovats analysis of 2,4-D like chemicals

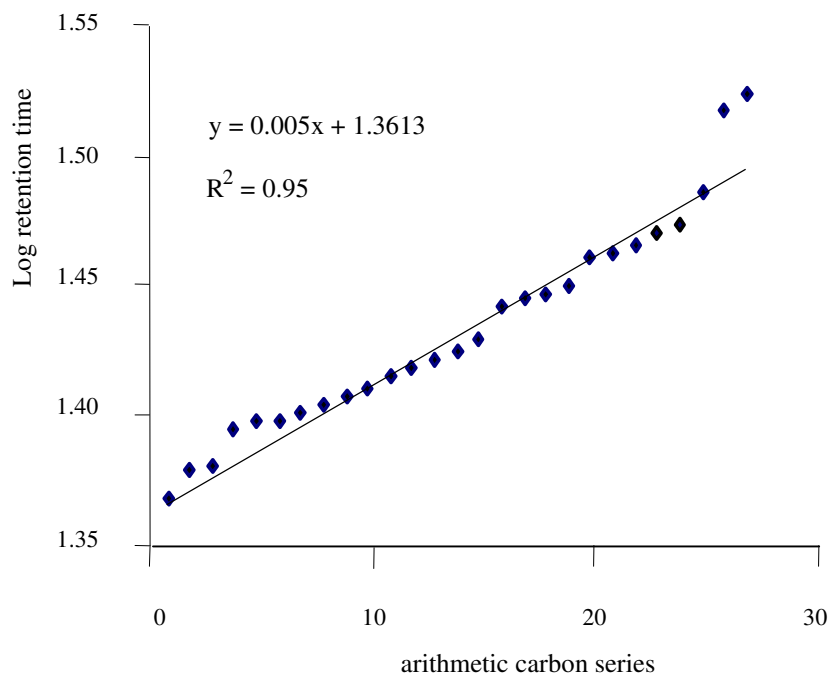
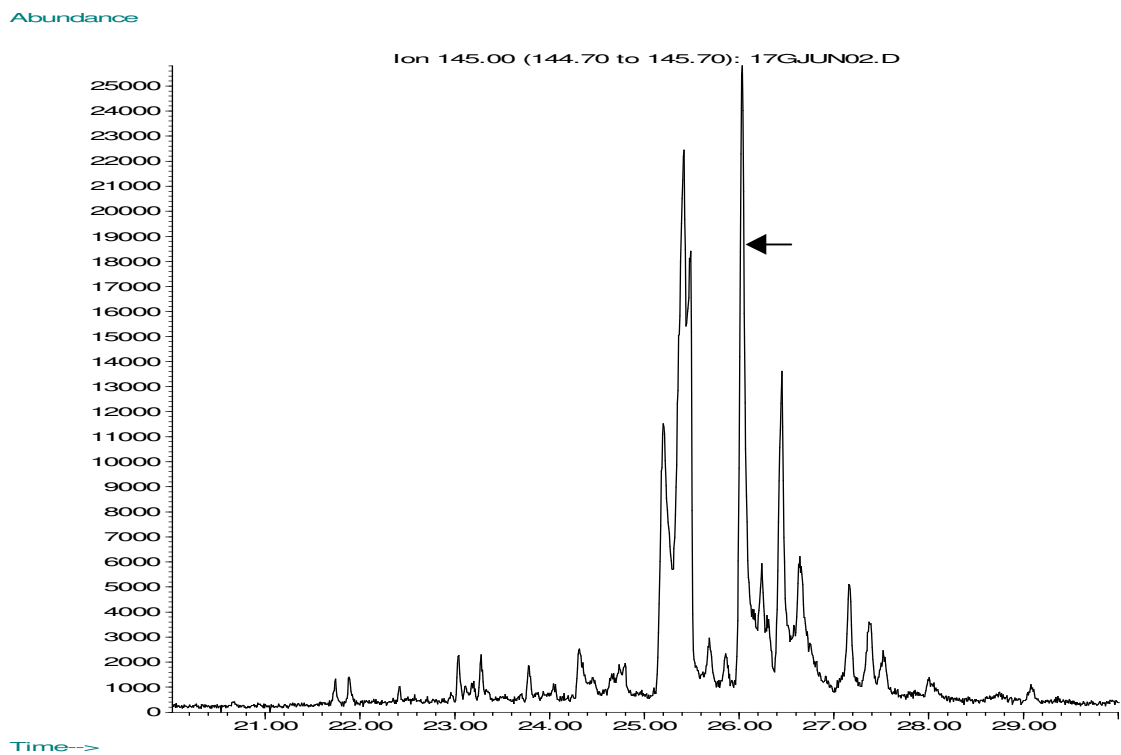
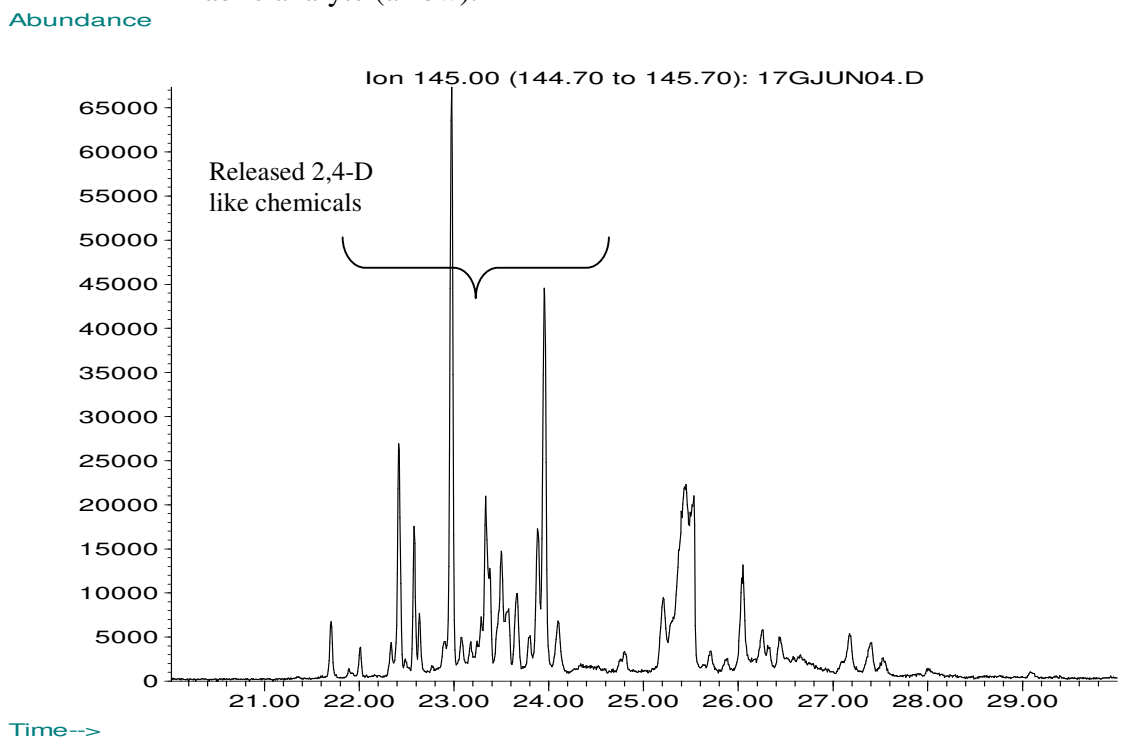


Figure A11: (continued).

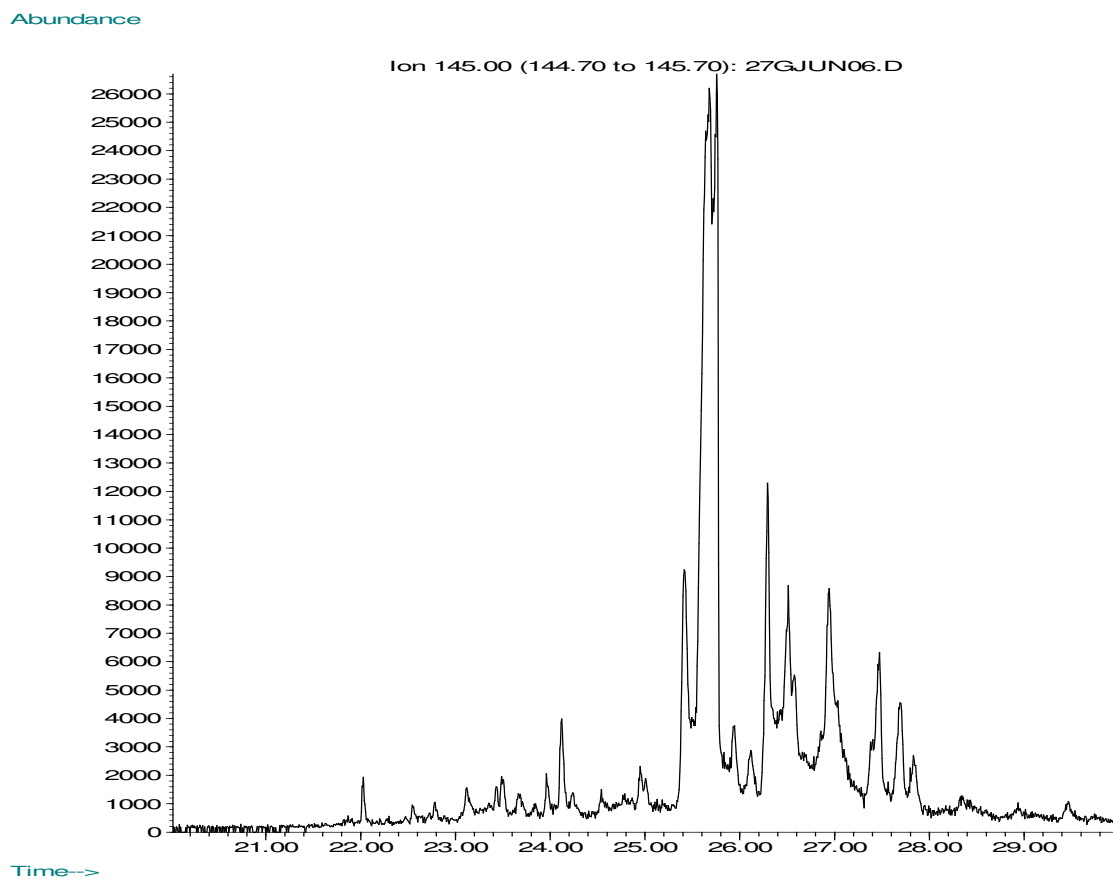


(a) Scan of an extract of whole soil #58 (no treatment) showing an acid-labile analyte (arrow).



(b) Scan of an extract of whole soil #58 (extracted ion $m/z = 145$) after an acid hydrolysis treatment

Figure A12: Scans of acid and alkali treatments of soil extracts.



- (c) Scan of an extract of whole soil #58 (extracted ion $m/z = 145$) after sequential treatments with acid then alkali.

Figure A12 (continued): Scans of acid and alkali treatments of soil extracts.

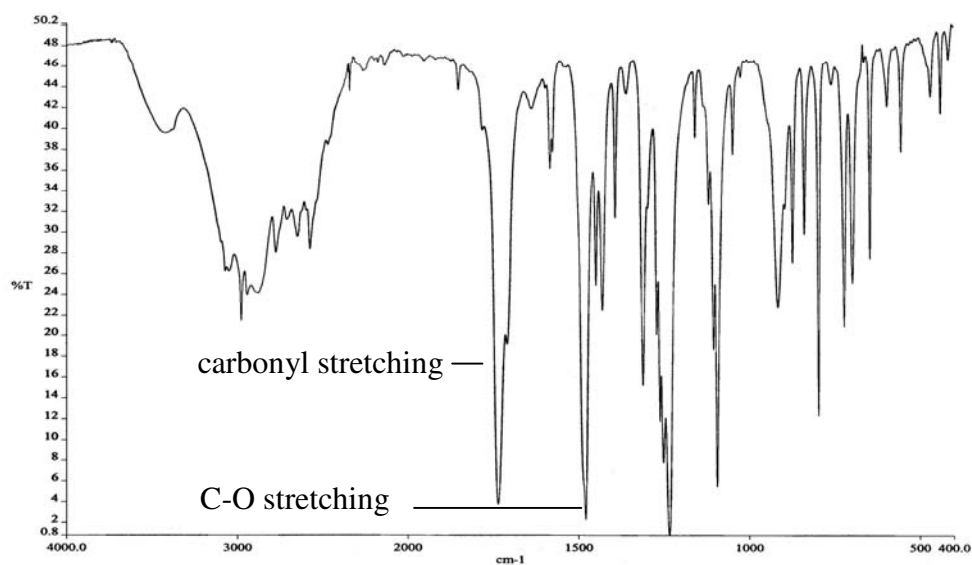


Figure A13: FTIR of isolated 2,4-dichlorophenoxyacetic acid

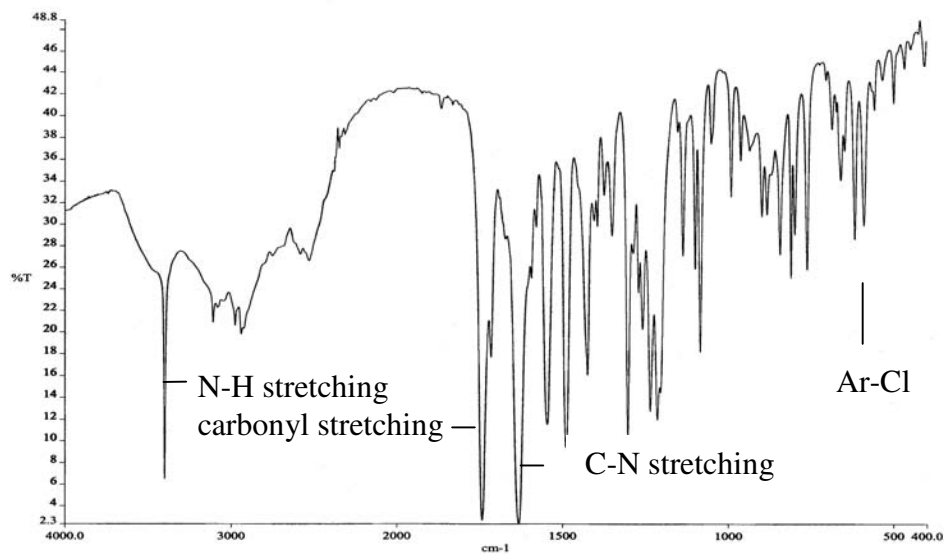


Figure A14: FTIR of an amino acid conjugate (2,4-D-asp) of 2,4-D.

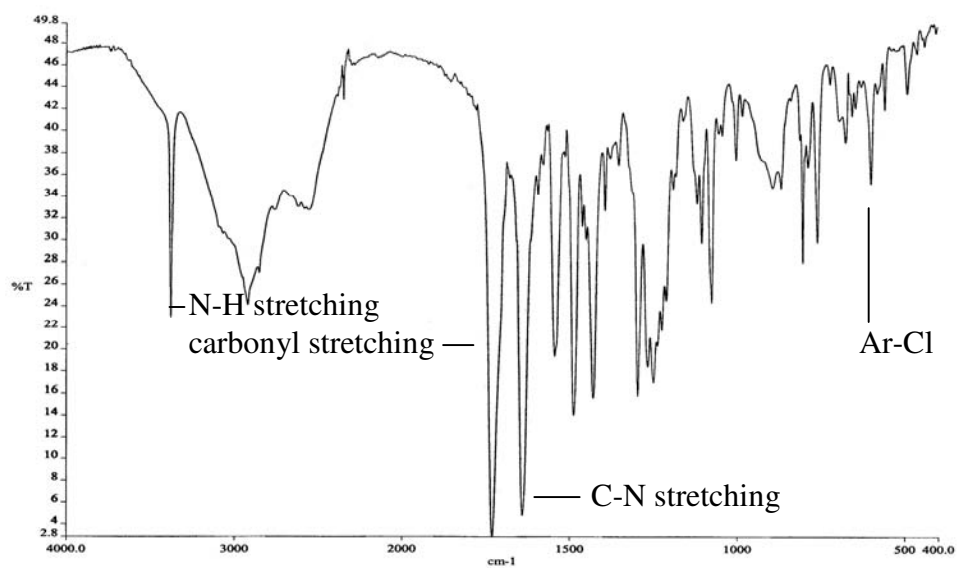


Figure A14 (continued): FTIR of an amino acid conjugate (2,4-D-glu) of 2,4-D.

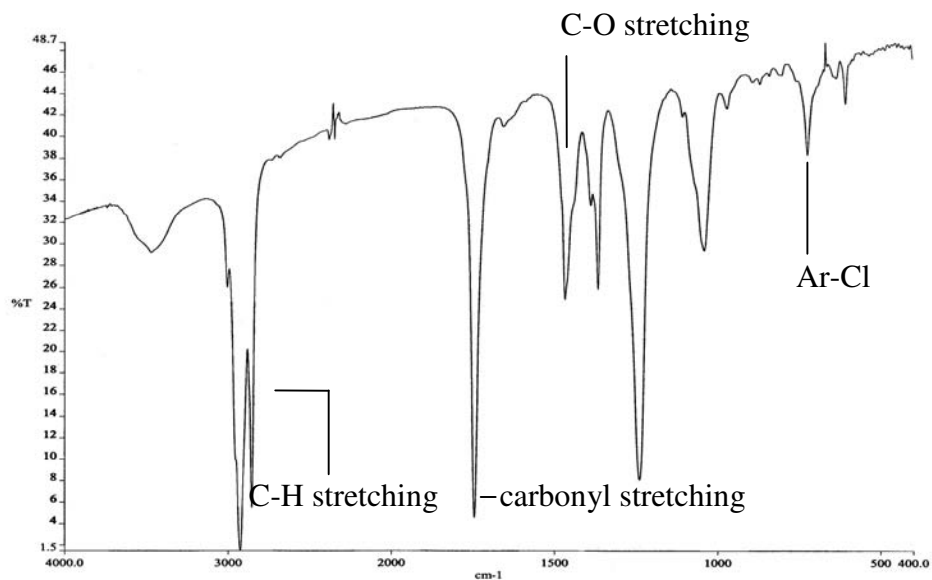


Figure A15: (a) The oleoyl ester of 2,4-dichlorophenoxyacetic acid

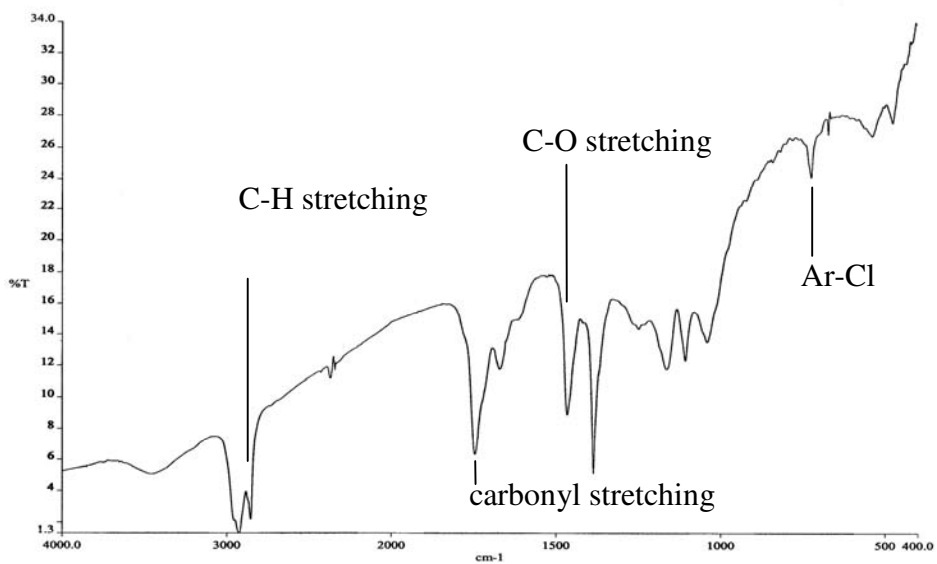
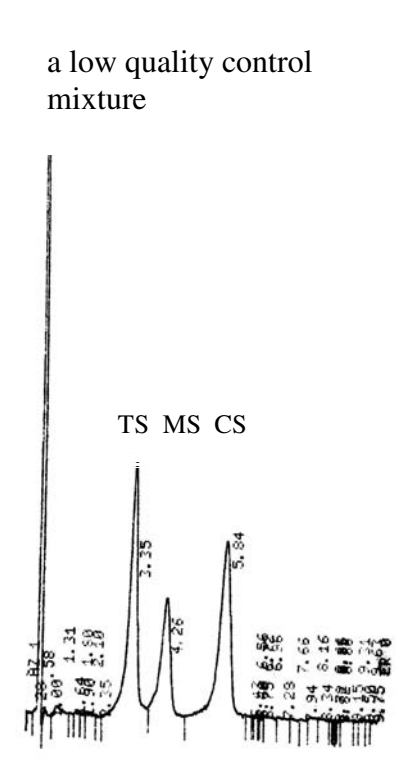
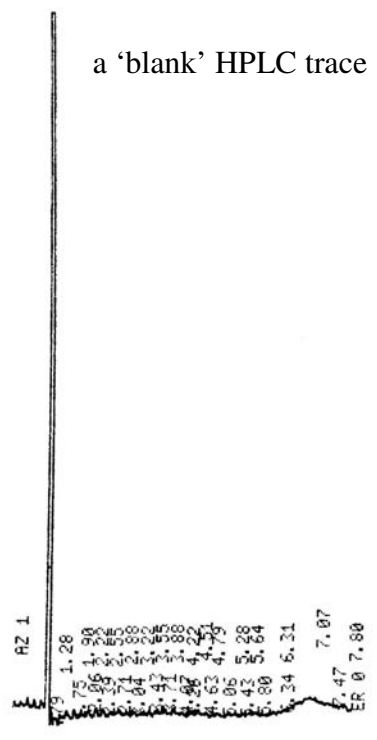


Figure A15: (b) Soil extract

Figure A15: FTIR of the oleoyl ester of 2,4-dichlorophenoxyacetic acid and a soil extract.



triasulfuron (TS), metsulfuron-methyl (MS) and chlorsulfuron (CS)

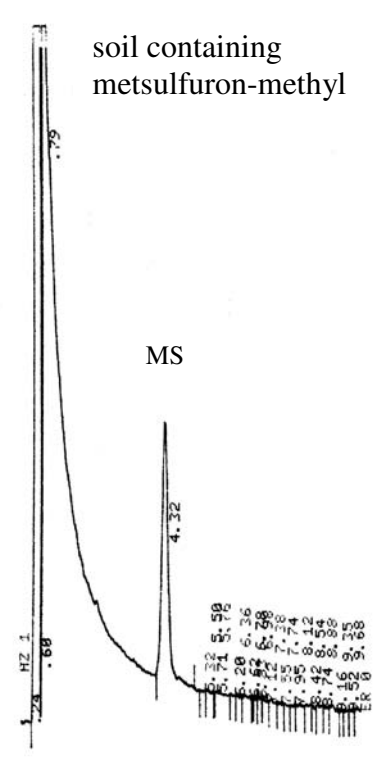
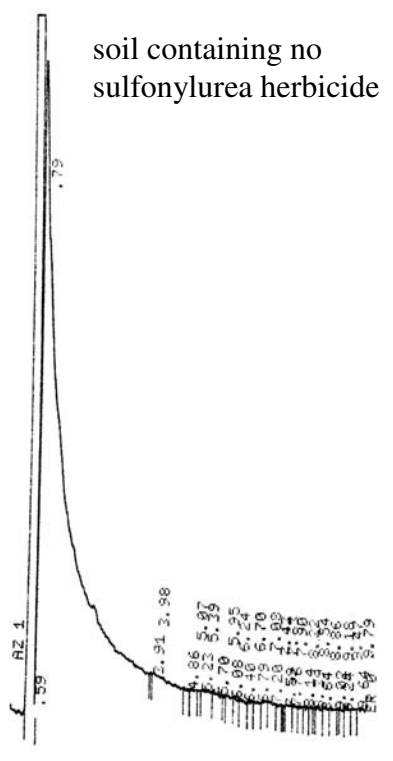


Figure A16: Sulfonylurea analysis of whole soils by HPLC

Appendix B

SIZE FRACTIONATION OF DRIED SOILS OF THE YORKE PENINSULA.

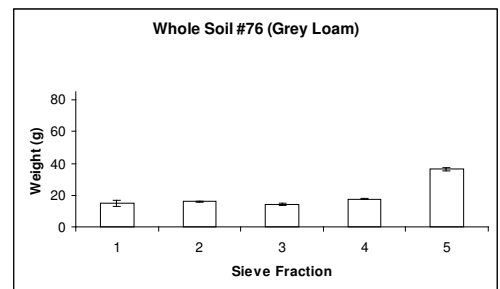
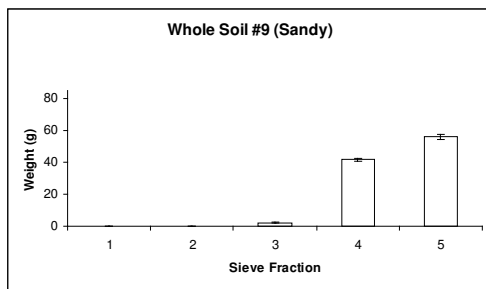
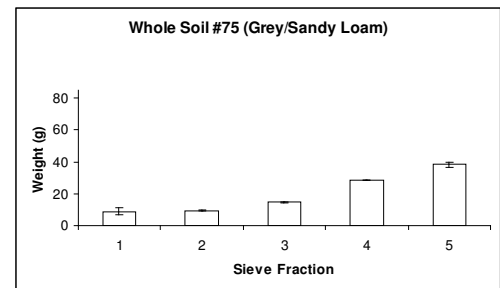
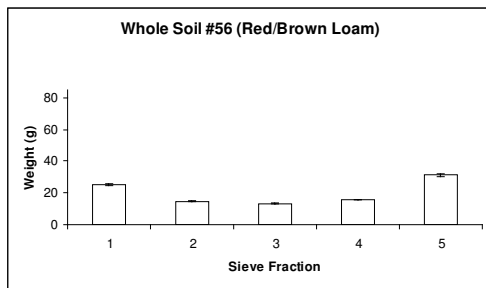
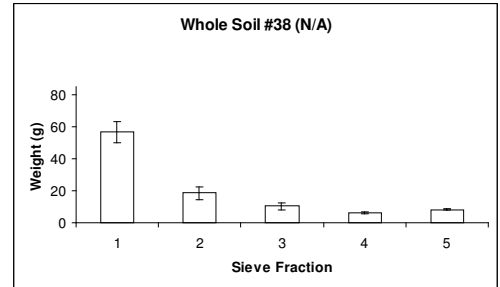
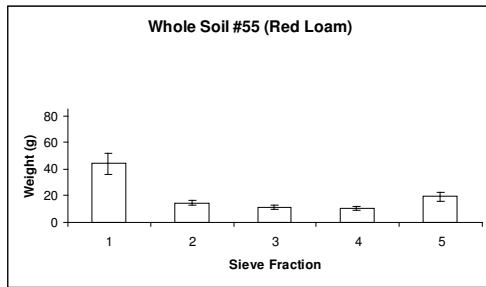
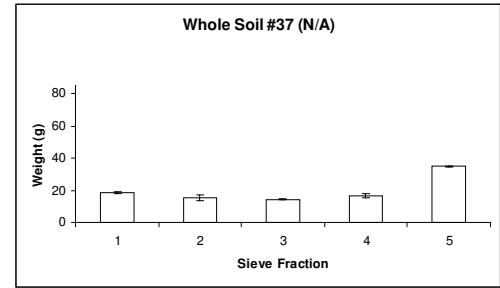
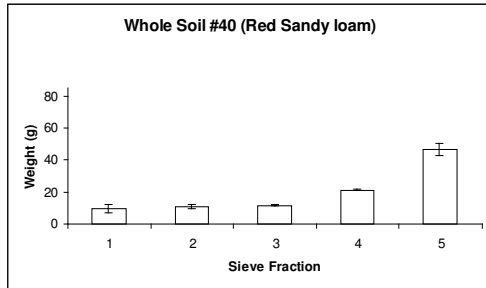
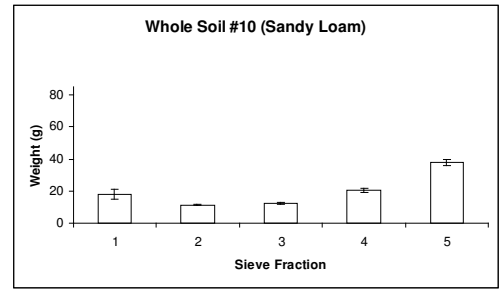
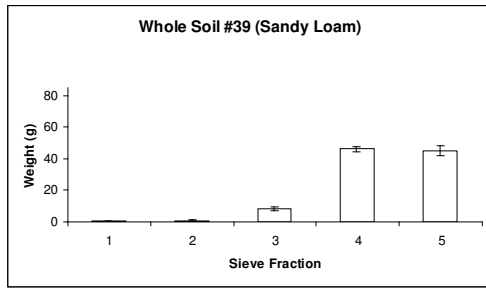


Figure B1: Size fractionation of dried soils of the Yorke Peninsula.

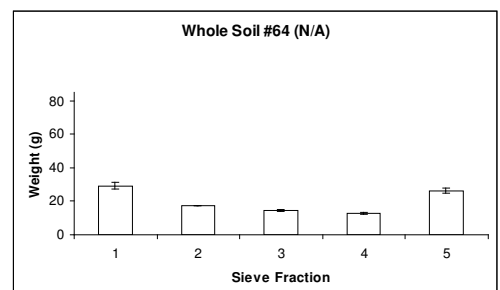
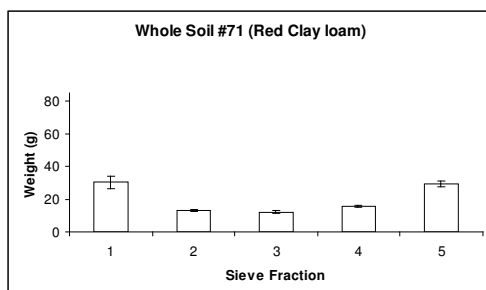
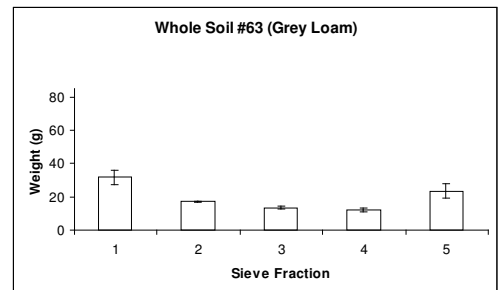
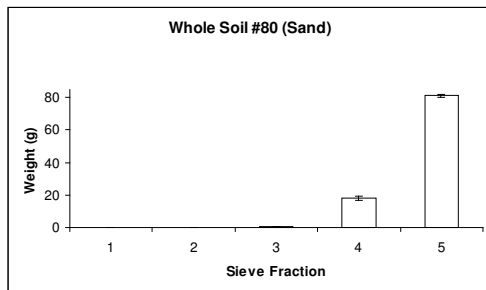
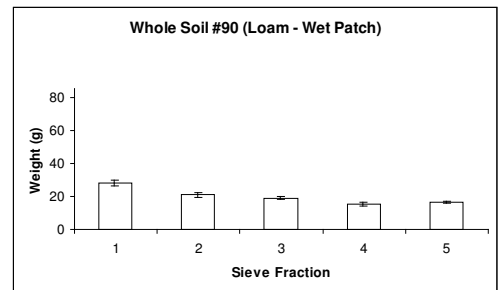
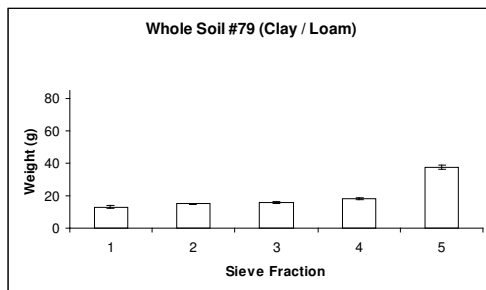
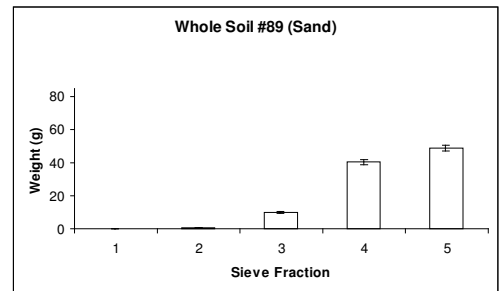
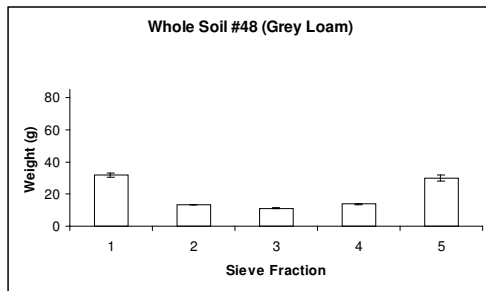
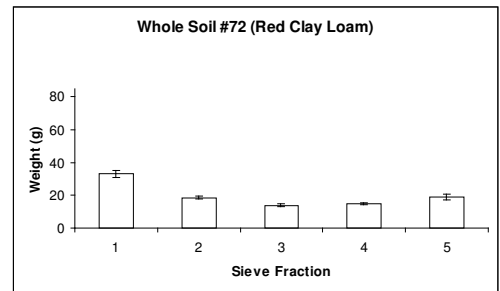
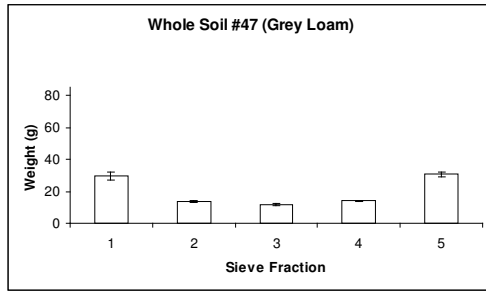


Figure B1 (continued): Size fractionation of dried soils of the Yorke Peninsula.

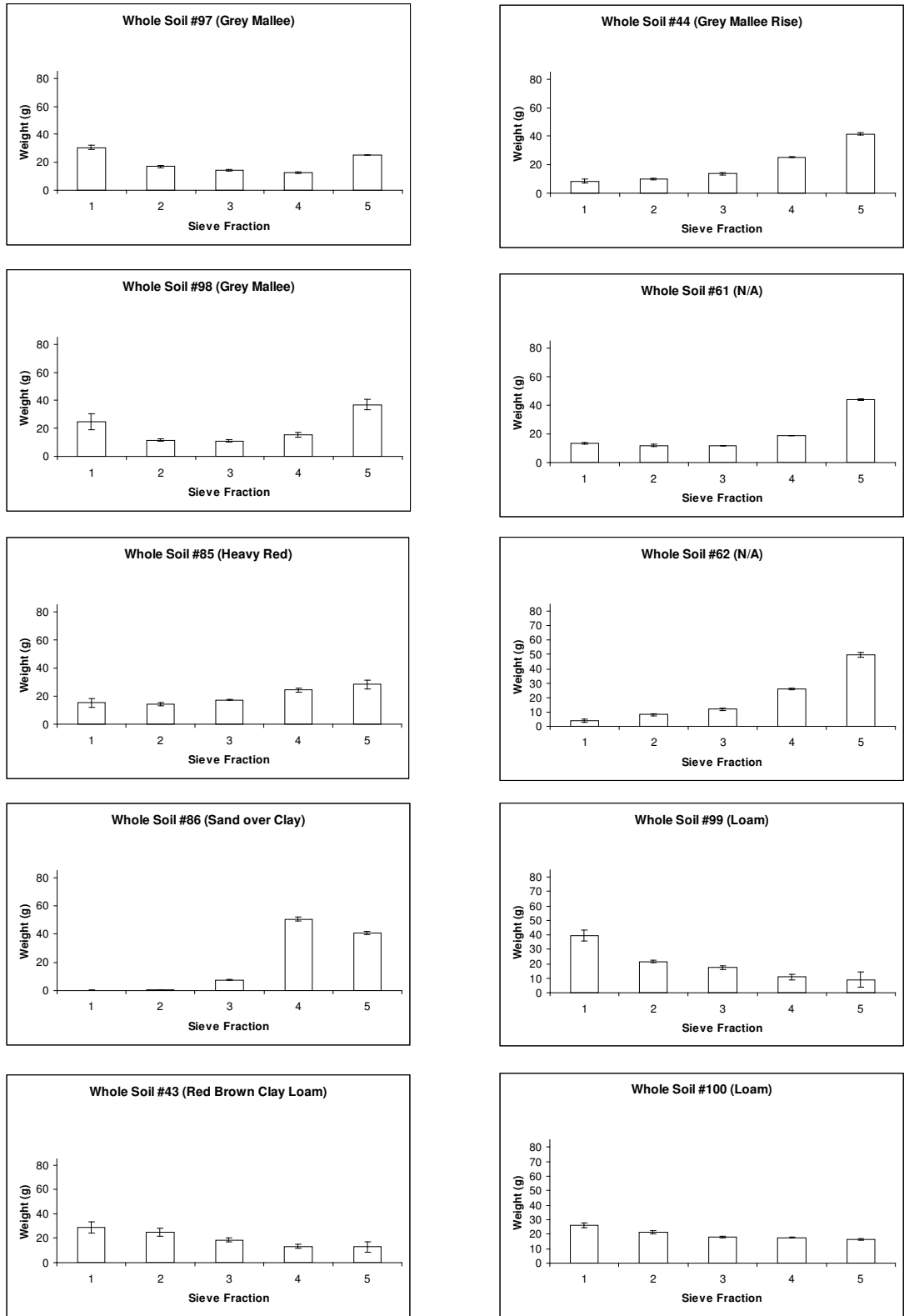


Figure B1 (continued): Size fractionation of dried soils of the Yorke Peninsula.

Soil ID#	Mean dry weights (g)					Standard deviation of dry weights (g)				
	x > 2 mm	1 mm < x < 2 mm	0.5 mm < x < 1 mm	0.25 mm < x < 0.5 mm	x < 0.25 mm	x > 2 mm	1 mm < x < 2 mm	0.5 mm < x < 1 mm	0.25 mm < x < 0.5 mm	x < 0.25 mm
	Fraction 1	Fraction 2	Fraction 3	Fraction 4	Fraction 5	Fraction 1	Fraction 2	Fraction 3	Fraction 4	Fraction 5
39	0	1	8	46	45	0	0	1	1	3
40	10	11	12	21	47	2	1	0	0	4
55	44	15	11	11	19	8	2	1	2	4
56	25	15	13	16	31	1	0	0	0	1
9	0	0	2	42	56	0	0	0	1	2
10	18	11	12	20	38	3	0	1	1	2
37	19	15	14	17	35	1	2	0	1	0
38	57	19	10	6	8	7	4	2	1	0
75	9	10	15	29	38	2	0	1	0	2
76	15	16	14	18	36	2	1	1	1	1
47	30	14	12	14	31	3	1	1	0	1
48	32	13	11	14	30	1	0	0	0	2
79	13	15	16	18	38	1	0	1	0	1
80	0	0	1	18	81	0	0	0	1	1
71	30	13	12	16	29	4	1	1	1	2
72	33	19	14	15	19	2	1	1	1	2
89	0	0	10	41	49	0	0	1	2	2
90	28	21	19	15	17	2	1	1	1	1
63	32	17	14	12	24	4	0	1	1	5
64	29	17	14	13	26	2	0	1	0	1
97	31	17	14	13	25	2	1	1	0	0
98	25	12	11	16	37	6	1	1	2	4

Table 1: Size fractionation of dried soils of the Yorke Peninsula.

Mean dry weights (g)						Standard deviation of dry weights (g)					
Soil ID#	x > 2 mm	1 mm < x < 2 mm	0.5 mm < x < 1 mm	0.25 mm < x < 0.5 mm	x < 0.25 mm	x > 2 mm	1 mm < x < 2 mm	0.5 mm < x < 1 mm	0.25 mm < x < 0.5 mm	x < 0.25 mm	
	Fraction 1	Fraction 2	Fraction 3	Fraction 4	Fraction 5	Fraction 1	Fraction 2	Fraction 3	Fraction 4	Fraction 5	
85	15	14	17	24	28	3	1	0	1	3	
86	0	0	8	51	41	0	0	0	1	1	
43	29	25	19	13	13	5	3	2	2	4	
44	9	10	14	25	42	1	0	1	0	1	
61	13	12	12	19	44	1	1	0	0	1	
62	4	8	12	26	50	1	1	1	0	2	
99	39	22	17	11	9	4	1	1	2	5	
100	26	21	18	18	16	2	1	0	0	0	

Table 1 (continued): Size fractionation of dried soils of the Yorke Peninsula.