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Characteristics and Sources of Organic Matter in Desert Sand Samples from the Riyadh and Al-Qasim Areas of Saudi Arabia: Preliminary Results

Abstract: Sand samples from the Riyadh and Al-Qasim areas were collected, extracted with a mixture of dichloromethane and methanol (3:1, v:v), and analyzed by gas chromatography-mass spectrometry (GC-MS) in order to characterize the contents and sources of their organic compounds. The major components of the total extracts were straight chain aliphatic compounds from vegetation waxes, fossil fuel combustion, and anthropogenic and agricultural activities. The results showed that anthropogenic inputs had a significant contribution to the organic content of sands near populated areas. This urban component consisted mainly of *n*-alkanes, *n*-alkanoic acids, *n*-alkyl amides, hopane and sterane biomarkers, and pesticide residues. Organic inputs from natural sources included *n*-alkanes, *n*-alkanoic acids, *n*-alkanols, methyl alkanoates, sterols, and *n*-alkanones.

Keywords: Desertsand, Organic contents, sources and characteristics, Saudi Arabia, Aliphatic, *n*-alkanes, sterane biomarkers, sterols, *n*-alkanones.

Introduction

The occurrence of biogenic and anthropogenic organic chemicals, which vary seasonally, is related to various sources in urban and rural regions (Aboul-Kassim and Simoneit, 1996; Beak *et al.*, 1991; Buehler *et al.*, 2001; Eganhouse *et al.*, 1981; Eglinton *et al.*, 1975; Fraser *et al.*, 1997; 1998a,b; Mazurek and Simoneit, 1984; Menichini, 1992; Morrison, 1969; Rogge *et al.*, 1993a,b, 1996; Simoneit, 1977a,b, 1978, 1982; 1984, 1986, 1989, 1998; Simoneit and Mazurek, 1989; Simoneit *et al.*, 1988, 1990, 1991a,b,c, 1993). Their concentrations in ecosystems, therefore, reflect the natural

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صفات و مصادر المادة العضوية في عينات رملية صحراوية من منطقتي الرياض والقصيم في المملكة العربية السعودية: نتائج أولية

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المستخلص: تم في هذا البحث إستخلاص المادة العضوية من عينات رملية جمعت من منطقتي الرياض والقصيم في المملكة العربية السعودية وذلك بإستخدام مخلوط من محلولي الكلورومثين الثنائي والميثانول بنسبة 1:3 بالحجم. تم تحليل المستخلص العضوي بواسطة جهاز الغاز الكروماتوغرافي مع مقياس طيف الكتلة لتعيين محتويات المركبات العضوية ومصادرها. برهنت النتائج أن معظم مركبات المستخلص العضوي عبارة عن سلسلة أليفاتية من شموع النباتات والمحروقات الوقودية والنشاطات البشرية والزراعية. كما بينت النتائج أن إضافات النشاطات البشرية لمحتويات الرمل واضحة، خصوصاً بالقرب من الأماكن الأهلة بالسكان. هذه الإضافات عبارة عن ألكينات وأحماض وأميدات وهوبيينات وستيرينات حيوية وبقايا موبيدات. أضافات المركبات العضوية من المصادر الطبيعية تضم ألكينات وأحماض وكحوليات وأسترات وأستيرويدات والكانونات.

كلمات مدخلية: رمال صحراء، مواد عضوية، المصادر والصفات، السعودية، سلسلة أليفاتية، الكينات، ستيرينات حيوية، أستيرويدات، الكانونات

background, human and biological activities, climate conditions, and physical features of the substrates.

The characterization and identification of the molecular composition of the organic matter in sands, soils, aerosols, and aquatic systems are important for understanding the nature of the components and assessing their potential toxic effects to human health. This is important because certain compound classes such as polycyclic aromatic hydrocarbons (PAHs), oxygenated PAHs (oxy-PAHs) and nitroPAHs produce detrimental health effects and can be found in soil, water and food (e.g., Alsberg *et al.*, 1985; Choudhury, 1982; Hannigan *et al.*, 1998; Simoneit, 1984; Westerholm *et al.*, 1988; 1991). Also, characterization of anthropogenic organic residues such as PAHs or pesticides may serve to further define and elucidate the spatial variation and geographical sources of organic burdens in urban versus rural areas (Eglinton *et al.*, 1975; Simoneit, 1982). Thus, the determination of the identities of organic

compounds, their amounts, their sources, and the compound classes is essential for environmental assessment processes.

Data concerning the major environmental problems that result from local and regional anthropogenic activities and the meteorological conditions which dominate over the major cities of Saudi Arabia are still lacking. The Riyadh and Al-Qasim areas are considered typical locations for assessing the composition of environmental organic matter, because they receive source input mixtures from local activities and long range atmospheric dust transport. The characterization of organic constituents in sands with respect to their natural and anthropogenic sources will facilitate an understanding of their local and regional impacts.

Since no research has been carried out to date to assess the organic matter contents and compositions of sands around the Riyadh City and Al-Qasim areas, this study is considered to be a first attempt to investigate and characterize the organic components and their sources in sand samples from these two areas.

Experimental Methods

1- Sampling and Extraction Procedure

Three sand samples were collected from the Riyadh and Al-Qasim areas in Saudi Arabia to determine their organic matter content by gas chromatography-mass spectrometry (GC-MS) analysis. The locations of the collected sand samples are shown in Figure 1. The R₁ sand sample was collected about 50 km northeast of Riyadh City, where only sand dunes were dominant and no vegetation was observed. The Q₁ sand sample was collected about 5 km southwest of Buraydah town (Salimiah, Al-Qasim area), whereas the Q₂ sample was collected from the city center of Buraydah. Each sample was sieved to obtain very fine particles (125µm) before total organic matter extraction. The extraction was performed twice by adding a mixture of methylene chloride/methanol (3:1 v/v) to the sieved fine particles of each sand and then ultrasonicated for 20 minutes before solvent collection. Each total extract was then concentrated under nitrogen blow-down and room temperature to approximately 50 µL before GC-MS analysis.

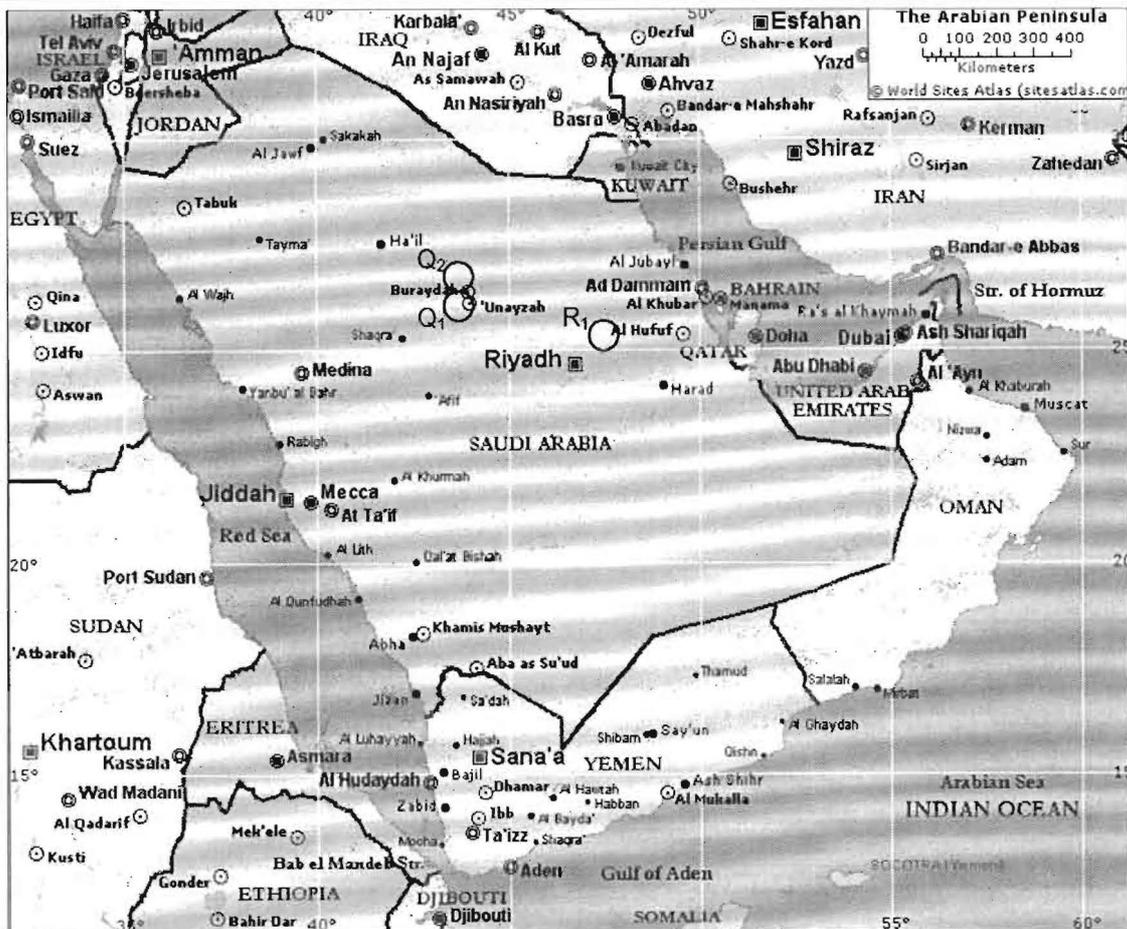


Figure 1: Map showing the locations of the collected sand samples

The total extracts of Riyadh and city center of Buryadah were separated by thin layer chromatography (TLC) on silica gel G plates (*Analtech, Inc.*) following the method described by Leif and Simoneit (1995). The plates were cleaned prior to use with solvent elutions and activated at 140° C for 45 min. After application of sample and elution standard, the TLC plates were developed with a mixture of heptane and diethyl ether (9:1). No fluorescence was detected under UV illumination of the dried plates, which were then exposed to iodine vapor to display the bands of the different fractions. The following five fractions were scraped off:

- (1) F1 (hydrocarbons),
- (2) F2 (monoaromatics, esters, ethers),
- (3) F3 (carbonyls, aromatics),
- (4) F4 (alcohols), and
- (5) F5 (origin).

The fractions were eluted with dichloromethane or methanol depending on the polarity of the fraction. F1-F3 were analyzed by GC-MS without further derivatization. F4 and F5 were derivatized with silylating reagent [N,O-bis (trimethylsilyl) trifluoroacetamide, BSTFA, *Pierce Chemical Co*] before analysis by GC-MS. This derivatizing agent replaces the H in hydroxyl groups with a trimethylsilyl [(CH₃)₃Si, i.e. TMS] group.

2- Instrumental Analysis

The analysis of the extracts was carried out by GC-MS, using a Hewlett-Packard 6890 GC coupled to a 5973 Mass Selective Detector with a DB-5 (*J and W Scientific, Agilent*) fused silica capillary column (30 m x 0.25 mm i.d., 0.25µm film thickness) and helium as carrier gas. The GC was temperature programmed from 65° C (2 min initial time) to 300° C at 6° C min⁻¹ (isothermal for 20 min final time). The MS was operated in the electron impact mode at 70 eV ion source energy. Data were acquired and processed with a Hewlett-Packard ChemStation.

Mass spectrometric data were acquired and processed using the GC-MS data system and compounds were identified by GC retention index and MS comparison with authentic standards, literature and library data, and characterized mixtures. Unknown compounds were characterized by interpretation of the fragmentation pattern of their mass spectra. Relative concentrations of the compounds were estimated from ratios of GC peak areas.

Results

The total extract contents, compound identities, yields and parameters of the sand sample extracts are shown in Table 1 and Figure 2. The data demonstrated that the total extract components were a mixture of *n*-alkanes, *n*-alkanoic acids, methyl alkanoates, *n*-alkanols, *n*-alkanyl- and *n*-alkenyl amides, *n*-alkenyl nitriles, sterols, hopanes, plasticizers and residues of pesticides and other unknown compounds. *n*-Alkanes were found to range between C₁₈ and C₃₅ with a maximum concentration at C₂₉ for all samples (Fig. 3a). Their abundances varied, with the maximum total concentration found in the Buraydah sand samples. The odd numbers of *n*-alkanes were dominant and the carbon preference index (CPI) ranged between 1.15 and 2.92. *n*-Alkanoic acids were also detected in these samples, and ranged from C₈ to C₁₆ with a maximum concentration at C₁₆ (Fig. 3b). The even number of *n*-alkanoic acids were the major homologs of the series and the CPI (e/o) ranged between 3.11 and 12.43 (Table 1). Methyl alkanoates were found in all sand samples and ranged from C₁₄ to C₃₀ with methyl hexadecanoate the dominant compound of the series (Fig. 3c). *n*-Alkanols were also observed in these samples as shown in Figure 3d and Table 1. They varied in concentrations and only even carbon numbered homologs from C₁₆ to C₃₂ were detected. Octadecanol (C₁₈) was the dominant *n*-alkanol in the sample from Riyadh, whereas C₃₀ was the maximum in the Salimiah sample (Table 1).

Alkyl amides were found mainly in the sand sample of Riyadh and only minor traces were observed in other samples (Table 1, Fig. 3e). Sterols were also detected in all samples and included cholesterol, campesterol, and (-)sitosterol as illustrated in Figure 3f. Trace amounts of amyrin triterpenols were also observed in these samples (Fig. 3g) as well as *n*-alkanones (Fig 3h).

Series of organic biomarkers were present in these samples. For example, hopane biomarkers were found in the sample from Buraydah town (Figure 4a). They extend from C₂₇ to C₃₅ with a maximum concentration at C₂₉. Also, traces of steranes were detected in the latter sample and included C₂₇ to C₂₉ steranes and diasteranes with the typical isomer composition of petroleum (Fig. 4b). Pesticide residues were detected only in the sample from Buraydah (Fig. 4c).

Table 1. Composition and various parameters of solvent-extractable organic matter of sand samples from Saudi Arabia.

Compound	Composition	Relative Concentration			
		Riyadh M.W.	Salimiah (R1)	Buraydah (Q1)	CC Q2)
<i>n</i>-Alkanes					
Heptadecane	C ₁₇ H ₃₆	240	-	T	0.14
Octadecane	C ₁₈ H ₃₈	256	T	T	0.18
Nonadecane	C ₁₉ H ₄₀	268	-	T	0.16
Eicosane	C ₂₀ H ₄₂	282	-	T	0.35
Heneicosane	C ₂₁ H ₄₄	296	-	0.64	0.77
Docosane	C ₂₂ H ₄₆	310	-	0.89	0.34
Tricosane	C ₂₃ H ₄₈	324	-	T	0.33
Tetracosane	C ₂₄ H ₅₀	338	-	0.51	1.21
Pentacosane	C ₂₅ H ₅₂	352	T	0.58	1.54
Hexacosane	C ₂₆ H ₅₄	366	-	0.38	0.62
Heptacosane	C ₂₇ H ₅₆	380	T	0.73	1.11
Octacosane	C ₂₈ H ₅₈	394	-	0.50	1.51
Nonacosane	C ₂₉ H ₆₀	408	T	1.01	1.19
Triacontane	C ₃₀ H ₆₂	422	-	T	1.40
Hentriacontane	C ₃₁ H ₆₄	436	-	0.73	1.12
Dotriacontane	C ₃₂ H ₆₆	450	-	T	-
Total			0	5.98	11.97
CPI (o/e)			2.26	1.69	1.15
<i>n</i>-Alkanoic Acids					
Octanoic acid	C ₈ H ₁₆ O ₂	144	0.67	1.77	0.40
Nonanoic acid	C ₉ H ₁₈ O ₂	158	1.18	1.91	0.77
Decanoic acid	C ₁₀ H ₂₀ O ₂	172	T	0.80	0.07
Undecanoic acid	C ₁₁ H ₂₂ O ₂	186	T	T	-
Dodecanoic acid	C ₁₂ H ₂₄ O ₂	200	T	T	-
Tridecanoic acid	C ₁₃ H ₂₆ O ₂	214	T	1.05	-
Tetradecanoic acid	C ₁₄ H ₂₈ O ₂	228	0.55	0.58	-
Pentadecanoic acid	C ₁₅ H ₃₀ O ₂	242	-	T	-
Hexadecanoic acid	C ₁₆ H ₃₂ O ₂	256	8.67	35.56	2.6
Total			11.08	41.66	3.90
CPI (e/o)			6.85	12.43	3.11
Methyl Alkanoates					
Methyl tetradecanoate	C ₁₅ H ₃₀ O ₂	242	T	-	0.10
Methyl pentadecanoate	C ₁₆ H ₃₂ O ₂	256	T	T	0.35
Methyl hexadecanoate	C ₁₇ H ₃₄ O ₂	270	-	1.35	T
Methyl hexadecanoate	C ₁₇ H ₃₄ O ₂	270	3.83	9.36	2.81
Methyl heptadecanoate	C ₁₈ H ₃₆ O ₂	282	1.40	1.24	-
Methyl heptadecanoate	C ₁₈ H ₃₆ O ₂	284	1.03	T	-
Methyl octadecanoate	C ₁₉ H ₃₈ O ₂	296	1.20	2.58	1.23
Methyl octadecanoate	C ₁₉ H ₃₈ O ₂	298	2.49	3.26	0.96
Methyl nonadecanoate	C ₂₀ H ₄₀ O ₂	312	T	T	1.52
Methyl eicosanoate	C ₂₁ H ₄₀ O ₂	324	0.51	-	-
Methyl eicosanoate	C ₂₁ H ₄₂ O ₂	326	0.60	0.89	0.67
Methyl heneicosanoate	C ₂₂ H ₄₄ O ₂	340	T	T	0.47
Methyl docosanoate	C ₂₃ H ₄₄ O ₂	352	1.98	-	-
Methyl docosanoate	C ₂₃ H ₄₆ O ₂	354	0.78	0.74	1.80
Methyl tricosanoate	C ₂₄ H ₄₈ O ₂	368	T	T	1.02

Methyl tetracosanoate	$C_{25}H_{50}O_2$	382	T	0.81	1.96
Methyl pentacosanoate	$C_{26}H_{52}O_2$	396	T	T	-
Methyl hexacosanoate	$C_{27}H_{54}O_2$	410	T	0.58	-
Methyl pentacosanoate	$C_{28}H_{56}O_2$	424	T	T	-
Methyl octacosanoate	$C_{29}H_{58}O_2$	438	T	T	T
Total			13.64	20.81	12.89
<i>n</i>-Alkanols					
Dodecanol	$C_{12}H_{26}O$	186	3.98	T	T
Tetradecanol	$C_{14}H_{30}O$	214	1.97	T	T
Hexadecanol	$C_{16}H_{34}O$	242	2.64	0.47	0.14
Octadecanol	$C_{18}H_{38}O$	270	3.16	0.73	0.12
Eicosanol	$C_{20}H_{42}O$	308	T	T	1.04
Docosanol	$C_{22}H_{46}O$	326	-	T	T
Tetracosanol	$C_{24}H_{50}O$	354	T	0.40	0.82
Hexacosanol	$C_{26}H_{54}O$	382	T	0.92	1.05
Octacosanol	$C_{28}H_{58}O$	410	T	1.08	0.68
Triacontanol	$C_{30}H_{62}O$	438	T	1.71	0.57
Dotriacontanol	$C_{32}H_{66}O$	466	T	T	0.48
Total			9.98	4.52	4.90
Alkyl Amides					
Lauramide	$C_{12}H_{25}NO$	199	-	-	T
Myristamide	$C_{14}H_{29}NO$	227	-	-	-
Palmitamide	$C_{16}H_{33}NO$	255	-	-	-
Oleamide	$C_{18}H_{35}NO$	281	5.42	T	T
Stearamide	$C_{18}H_{37}NO$	283	0.96	-	-
Eicosenamide	$C_{20}H_{39}NO$	309	-	-	-
Erucamide	$C_{22}H_{43}NO$	337	14.79	-	-
Total			21.17	0	0
Alkenyl Nitriles					
Docosenyl nitrile	$C_{22}H_{41}N$	319	4.84	-	-
Total			4.84	0	0
Steroids					
Cholesterol	$C_{27}H_{46}O$	386	0.64	0.55	0.70
Campesterol	$C_{28}H_{46}O$	400	0.40	-	0.30
Stigmasterol	$C_{29}H_{48}O$	412	-	-	0.60
β -Sitosterol	$C_{29}H_{50}O$	414	0.42	-	0.34
Total			1.45	0.55	1.94
Sugar Derivatives					
Levogluconan	$C_6H_{10}O_5$	162	-	-	T
Mannosan	$C_6H_{10}O_5$	162	-	-	T
Galactosan	$C_6H_{10}O_5$	162	-	-	T
Total			0	0	0
<i>n</i>-Alkan-2-ones					
Dodecan-2-one	$C_{12}H_{24}O$	184	-	-	0.05
Tridecan-2-one	$C_{13}H_{26}O$	198	-	-	0.08
Tetradecan-2-one	$C_{14}H_{28}O$	212	-	-	0.08
Pentadecan-2-one	$C_{15}H_{30}O$	226	-	T	0.15
Hexadecan-2-one	$C_{16}H_{32}O$	240	-	T	0.10
Heptadecan-2-one	$C_{17}H_{34}O$	254	-	T	0.14
Octadecan-2-one	$C_{18}H_{36}O$	268	-	-	0.02
Nonadecan-2-one	$C_{19}H_{38}O$	282	-	-	0.03

Eicosan-2-one	$C_{20}H_{40}O$	296	-	-	0.07
Heneicosan-2-one	$C_{21}H_{42}O$	310	-	-	0.08
Docosan-2-one	$C_{22}H_{44}O$	324	-	-	0.05
Total			0	0	0.85
6,10-Dimethylundecan-2-one	$C_{13}H_{26}O$	198	-	-	0.21
6,10,14-Trimethylpentadecan-2-one	$C_{18}H_{36}O$	268	-	-	0.03
Hopane Biomarkers					
Trisnorhopane	$C_{27}H_{46}$	370	-	-	0.71
17 α (H)-Trisnorhopane	$C_{27}H_{46}$	370	T	-	0.63
17 α (H),(H)-Norhopane	$C_{29}H_{50}$	398	-	-	1.90
17 α (H),21 β (H)-Hopane	$C_{30}H_{52}$	412	T	-	0.79
17 α (H),21 β (H)-22S-Homohopane	$C_{31}H_{54}$	426	-	-	0.71
17 α (H),21 β (H)-22R-Homohopane	$C_{31}H_{54}$	426	-	-	0.51
Gammacerane	$C_{30}H_{52}$	412	-	-	0.47
17 α (H),21 β (H)-22S-Bishomohopane	$C_{32}H_{56}$	440	-	-	0.28
17 α (H),21 β (H)-22R-Bishomohopane	$C_{32}H_{56}$	440	-	-	0.22
17 α (H),21 β (H)-22S-Trishomohopane	$C_{33}H_{58}$	454	-	-	0.13
17 α (H),21 β (H)-22R-Trishomohopane	$C_{33}H_{58}$	454	-	-	0.11
17((H),21 β (H)-22S-Tetrakishomohopane	$C_{34}H_{60}$	468	-	-	0.05
17((H),21 β (H)-22R-Tetrakishomohopane	$C_{34}H_{60}$	468	-	-	0.07
17 α (H),21 β (H)-22S-Pentakishomohopane	$C_{35}H_{62}$	482	-	-	0.07
17 α (H),21 β (H)-22R-Pentakishomohopane	$C_{35}H_{62}$	482	-	-	0.04
Total			0	0	6.68
C_{31} S/(R+S)		-	-	-	0.58
C_{32} S/(R+S)			-	-	0.63
Steranes					
14 β ,17 β -20R-Cholestane	$C_{27}H_{48}$	372	-	T	1.86
14 β ,17 β -20R-24-Ethylcholestane	$C_{29}H_{52}$	400	-	T	
14 β ,17 β -20S-24-Ethylcholestane	$C_{29}H_{52}$	400	-	T	1.16
14 α ,17 α -20R-24-Ethylcholestane	$C_{29}H_{52}$	400	-	-	T
Total			0	0	3.02
Plasticizers/Antioxidants					
Diethyl phthalate	$C_{12}H_{14}O_4$	222	-	-	-
Dibutyl phthalate	$C_{16}H_{22}O_4$	278	3.37		0.47
Diocetyl phthalate	$C_{24}H_{38}O_4$	390	4.52	1.18	-
Diocetyl adipate	$C_{22}H_{42}O_4$	370	1.04	-	-
Triphenyl phosphate	$C_{18}H_{15}P_4$	326	-	-	-
Total			8.93	1.18	0.46
Pesticides					
Dowicide 2S	C_6H_3O	91	-	-	0.36
Pendimethalin	$C_{13}H_{19}N_3O_4$	218	-	-	1.43
Iso-octyl-MCPA	$C_{17}H_{25}C_1O_3$	312	-	-	0.53
Methyl dichlorofop	$C_{16}H_{14}C_{12}$	340	-	-	0.11
Total			0	0	2.43
Squalene			1.13	0.43	-
UCM			23.75	20.41	52.68
U/R			0.46	0.28	1.14
Overall Total			95.97	95.54	98.87

M.W. = Molecular weight; - = not detected; T = trace (relative concentration <0.01);
 CPI(o/e) = $\sum(nC_{19} + \dots + nC_{33}) / \sum(nC_{18} + \dots + nC_{32})$; CPI(e/o) = $\sum(nC_{10} + \dots + nC_{16}) / \sum(nC_9 + \dots + nC_{15})$;
 UCM = unresolved complex mixture; U/R = unresolved to resolved components

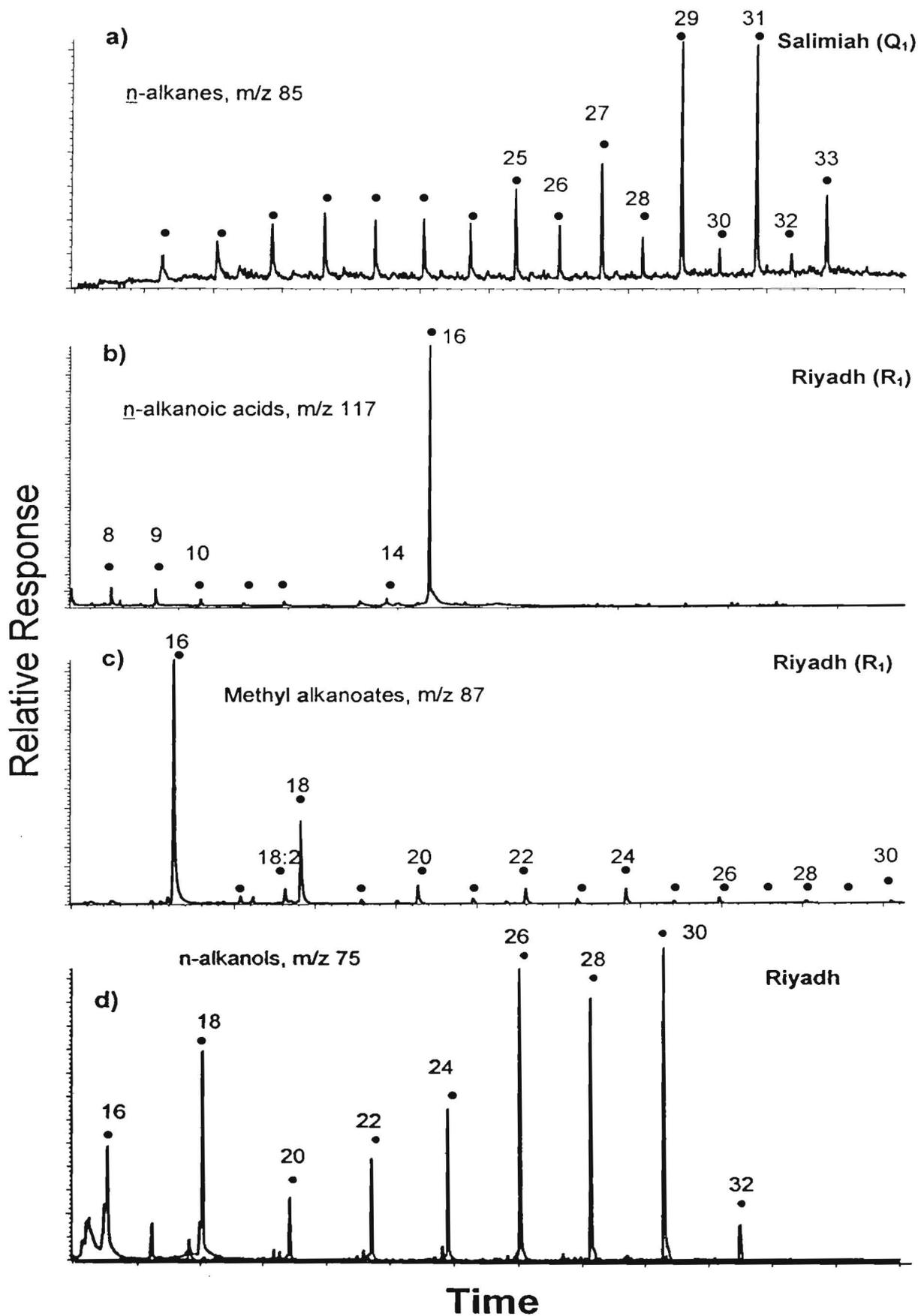


Figure 3: GC-MS key ion plots of various compound series found in the sand samples: a) n-alkanes; b) n-alkanoic acids; c) methyl alkanoates; d) n-alkanols

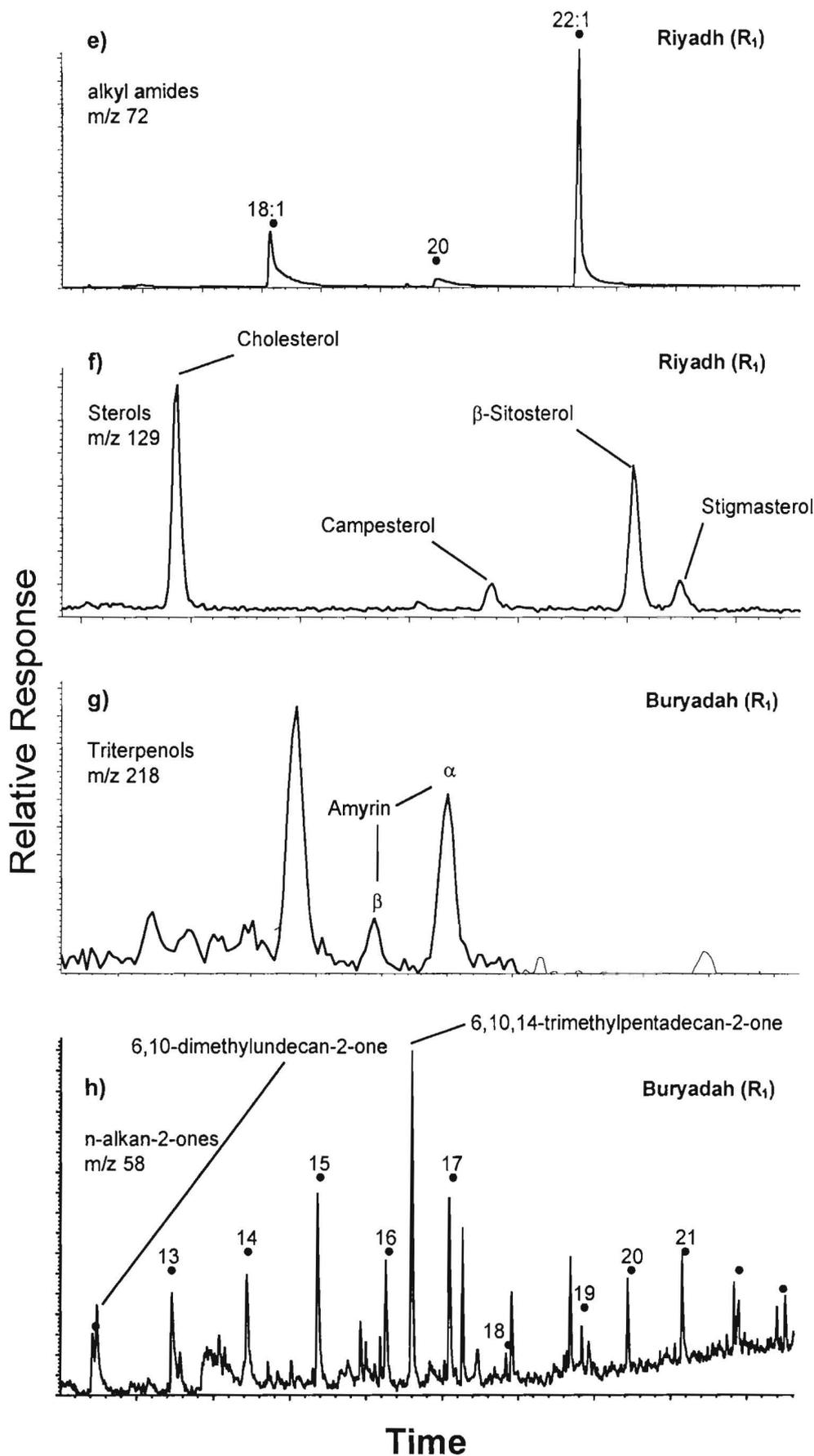


Figure 3 contd.: GC-MS key ion plots of various compound series found in the sand samples: e) alkyl amides; f) sterols; g) triterpenols; and h) n-alkan-2-ones

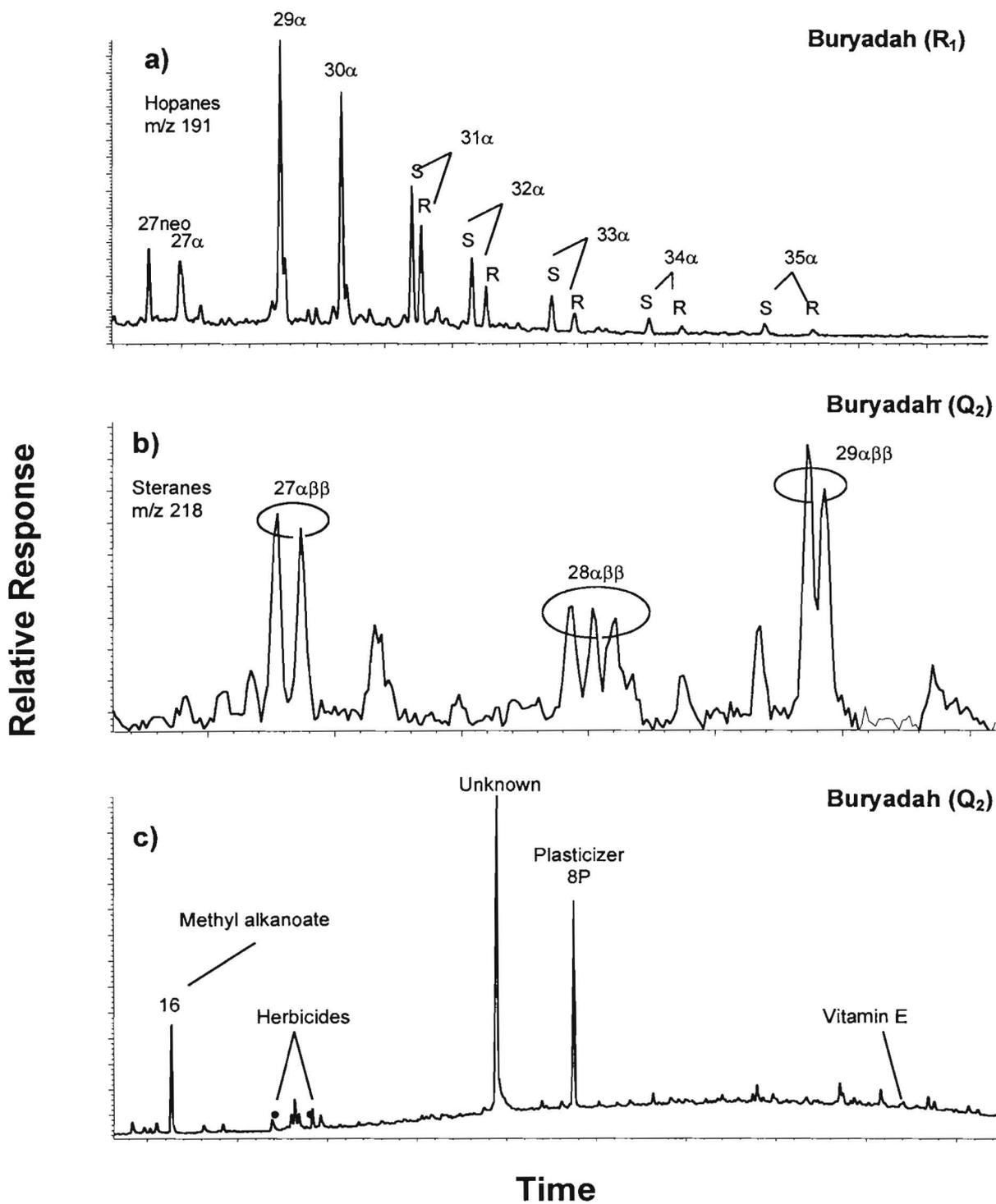


Figure 4: GC-MS key ion plots of biomarkers and herbicides in the sand samples: a) hopanes; b) steranes; and; c) herbicides

Discussion

The chemical analysis of the sand samples indicates two sources of the organic matter. These are natural background from surrounding regional vegetation and anthropogenic sources from urban and agricultural activities and vehicle emissions.

The natural sources are indicated by the occurrence of *n*-alkanes, *n*-alkanoic acids, *n*-alkanols, methyl alkanooates and sterols. They are mainly from higher plant biomass. This is shown by the presence of *n*-alkanes with an odd carbon number preference ($CPI(o/e) > 1$) and carbon number maximum mainly at 29 and/or 31 (see Table 1, e.g., see Fig 3a), which indicates an origin from higher plant waxes (Simoneit, 1977a,b; 1989). The long chain *n*-alkanols and *n*-alkanoic acids in the extractable lipids or bound in the complex organic matter (e.g., as part of membrane residues) can be another indicator for a biomass origin. The presence of *n*-alkanoic acids and *n*-alkanols with an even carbon number predominance, as shown in Figure 3b and 3d, is thus a result of higher plant biomass input, as well as microbial alteration of the organic matter in the sand samples. The *n*-alkanoic acids with a strong even carbon number predominance ($CPI(e/o) = 3.1$ to 12.4, see Table 1) are found in all samples and indicate a biotic origin. They have a carbon number maximum at 16, and derive from multiple sources including plant cutin and suberin (Holloway, 1982). The presence of nonanoic acid (C_9) in all samples is interpreted as an indicator for the oxidation of elaidic and oleic acids from lipids. The even *n*-alkanols ranging from C_{18} to C_{30} and a carbon number maximum at 18 or 30 indicate that they are of a vascular plant wax origin (Simoneit, 1977a,b; 1989). The presence of steroidal alcohols (sterols) in these samples also indicates a natural source. They are found in the sample from the Buraydah area and ranged from C_{27} (cholesterol) to C_{29} (sitosterol) (see Fig 3f). The general sterol distribution for the samples analyzed shows a cholesterol and β -sitosterol dominance, with campesterol and stigmasterol as minor compounds. These sterols are likely to have an origin from algae and vegetation (e.g., Barbier *et al.*, 1981; Simoneit *et al.*, 1983). Triterpenoids including α -amyrin and β -amyrin also from higher vascular plant waxes are present at trace amounts (see Fig. 3g).

The concentrations of aliphatic ketones are low in all samples. They consist of *n*-alkan-2-ones ranging from C_{12} to C_{16} , with an odd carbon number predominance and carbon number maximum at 16,

and 6,10-dimethylundecan-2-one and 6,10,14-trimethylpentadecan-2-one (see Fig. 3h). The *n*-alkanones are indicators for a vegetation input and may form by microbial processes from plant wax lipids (e.g., Morrison and Bick, 1967; Oros *et al.*, 1999). The major amount of isoprenoidal ketones (e.g., 6,10,14-trimethylpentadecan-2-one), which are also present in these samples, is interpreted to derive from both bacterial alteration and photochemical oxidation of the isoprenoidyl side chain of chlorophyll a (Brooks and Maxwell, 1974; Grossi *et al.*, 1998).

The anthropogenic inputs are obvious and are indicated by the occurrence of petroleum biomarkers (e.g., hopanes and steranes, see Fig 4a, b), alkyl amides, alkenyl nitriles, pesticide residues, series of fossil fuel *n*-alkanes and UCM (unresolved complex mixture of branched and cyclic hydrocarbons), and plasticizers (see Table 1). The presence of the biomarker hopanes and steranes in the sample from Buraydah confirms the contribution from petroleum combustion. The UCM (see Table 1, Figure 2) is the major petroleum component derived from lubricating oil in vehicle emissions, which is indicated by the high value of U/R index (= 1.14, see Table 1). However, these petroleum compounds are not detected in the other samples. Organic compound inputs from cooking processes are also indicated by the presence of alkyl amides and alkenyl nitriles in all samples (see Table 1), with greatest amounts in the sample from the Riyadh area. The alkenyl nitriles were found only in the Riyadh area. The absence of significant concentrations of PAHs indicates that organic compounds from combustion processes are not of a major input.

An important finding is the detection of pesticide residues in the samples from the Buraydah area. They are Dovicide 2S, Pendimethalin, Methyl dichlorofop and iso-octyl-MCPA (Fig. 5), all herbicides used in the area. They may be transported by dust and accumulated in this area or derive from spills at local pesticide stores. The presence of plasticizers and antioxidants (see Fig.4c) is attributed to contamination from plastic sample bags. The total anthropogenic inputs are estimated to range from 34 to 75% of the total extractable organic content of the sand samples.

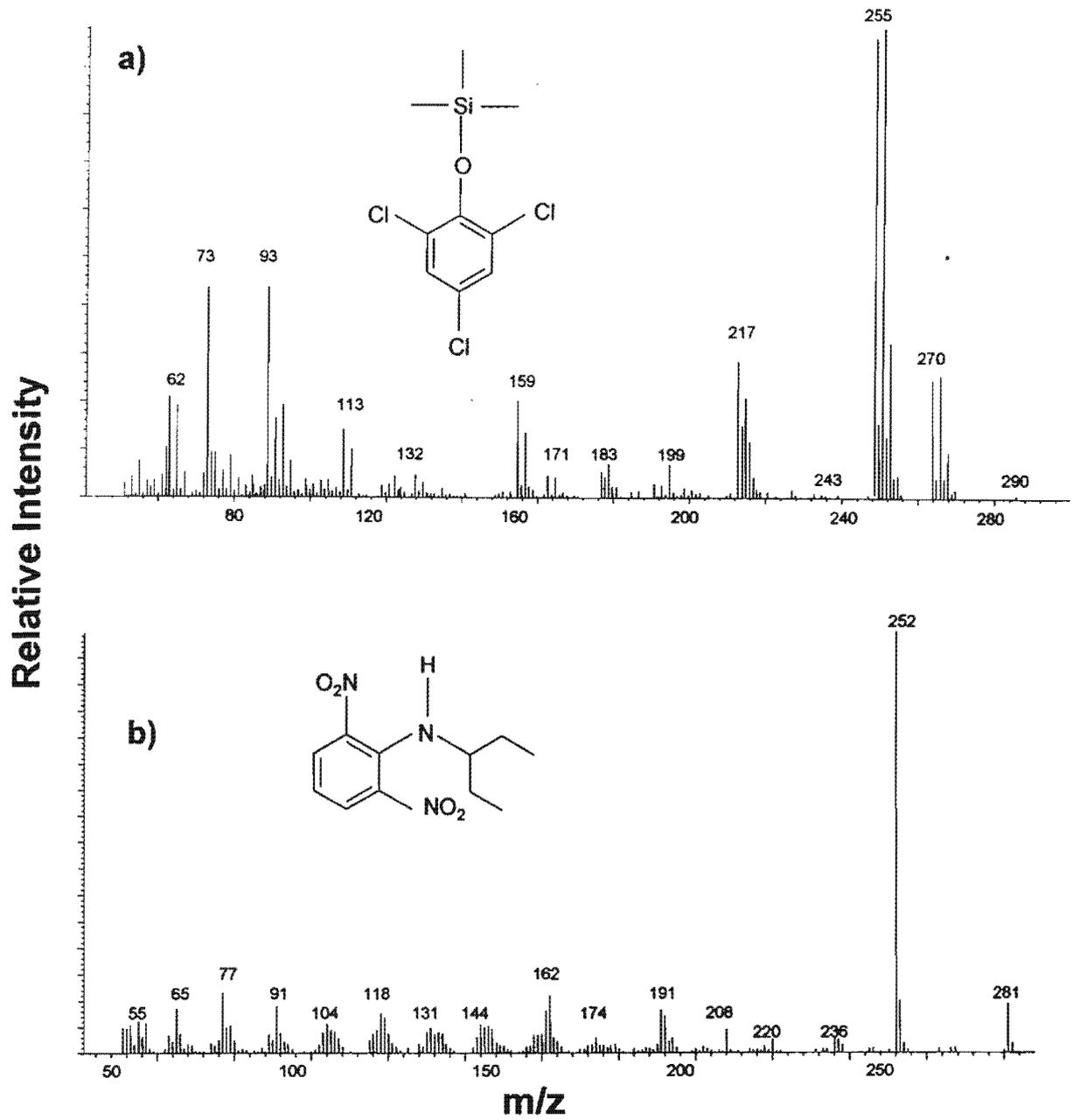


Figure 5: Mass spectra of herbicides detected in the Buraydah sand sample: a) Dowicide 2S; b) Pendimethalin; c) iso-octyl-MCPA; and d) Methyl dichlorofop

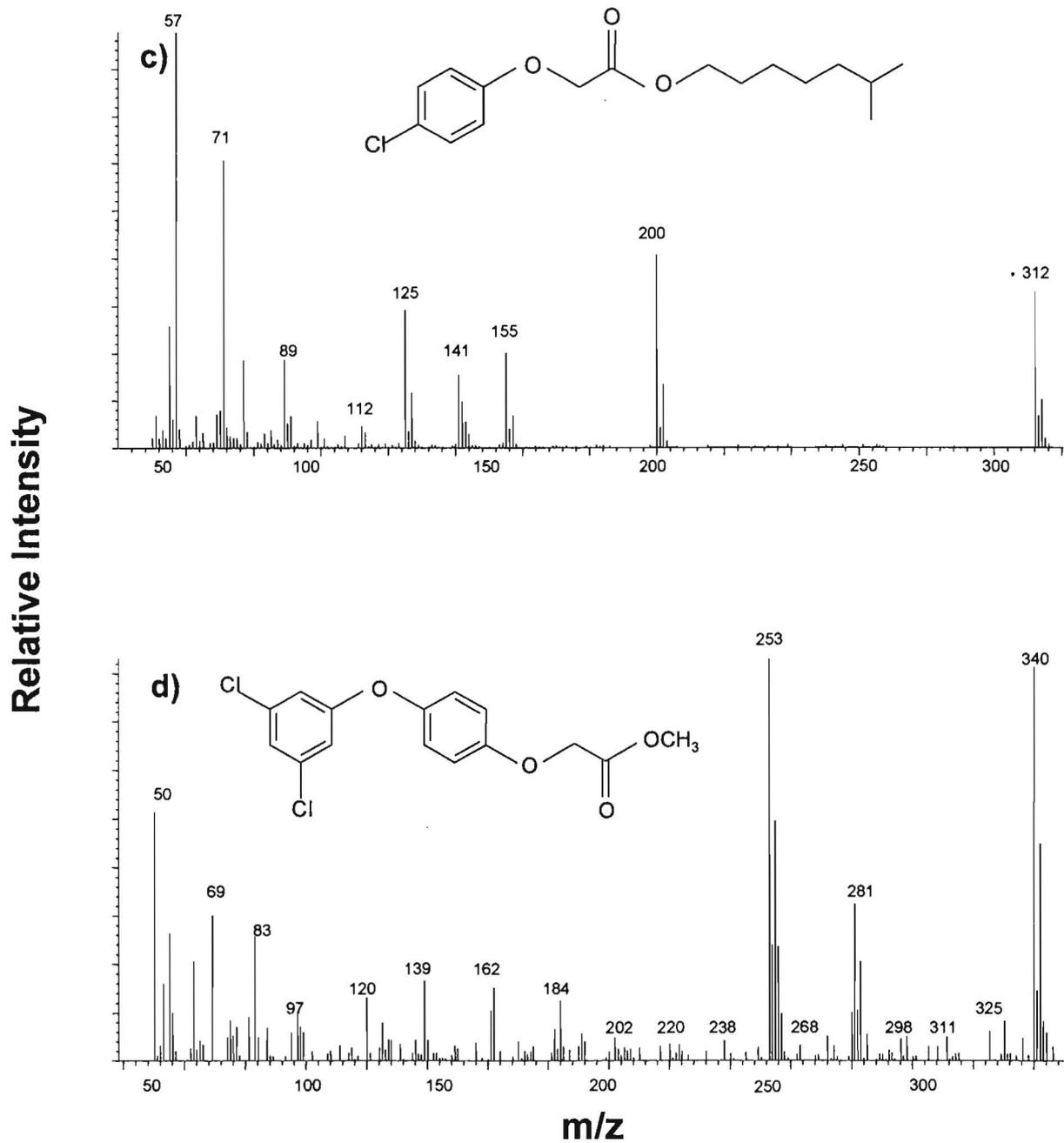


Figure 5: Mass spectra of herbicides detected in the Buraydah sand sample: a) Dowicide 2S; b) Pendimethalin; c) iso-octyl-MCPA; and d) Methyl dichlorofop

Conclusion

The chemical analyses of sand samples from the Riyadh and Al-Qasim areas show that anthropogenic sources are significant contributors to the organic content of the sands. These anthropogenic sources are characterized by the presence of *n*-alkanes with CPI ~ 1 (e.g., Buraydah area); hopane and sterane biomarkers and UCM from fossil fuel combustion; alkyl amides and alkenyl nitriles from cooking; plasticizers and antioxidants from sample bags; and importantly pesticide residues from agricultural activities. These anthropogenic sources comprise between 34 to 75% of the total extractable organic matter.

The natural sources of organic matter are mainly from vegetation (e.g., higher plant wax) and their contributions to the total extractable organic contents of the sands range from 25 to 66%. The organic compounds from natural sources include *n*-alkanes, *n*-alkanoic acids, *n*-alkanols, methyl *n*-alkanoates, sterols, triterpenoids and *n*-alkanones.

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