Arab Gulf Journal of Scientific Research, 22 (3), pp 165-172 (2004)

Original Paper Ref. No 2262

Occurrence of Pesticides and Herbicides in Soil and Sand Dust from Riyadh City, Kingdom of Saudi Arabia

وجود مبيدات حشرية ونباتية في غبار تربة ورمل مدينة الرياض - المملكة العربية السعودية

أحمد رشدي *، خالد المطلق و برند سيمونية

Ahmed I Rushdi*, Khalid Al-Mutlaq and Bernd RT Simoneit

*Environmental and Petroleum Geochemistry Group, College of Oceanic and Atmospheric Sciences, Oregon State University, Corvallis Oregon 97331, U.S.A.

* جامعة أوريجون - الولايات المتحدة الأمريكية

Abstract: Soil and sand dust resuspension is one of the major input mechanisms of harmful anthropogenic substances into the atmosphere of arid regions. Pesticides and herbicides are the major components of these toxic substances in soils of agricultural regions. This research examines the occurrence of pesticides and herbicides in soil and sand dust from various locations in the city of Riyadh, Kingdom of Saudi Arabia. The organic components, including pesticides, herbicides, fossil fuel residues, and natural lipids were analyzed by GC-MS for this area to define their sources and strengths. The results show that various pesticides and herbicides are present in soil and sand dust in Riyadh City and include Carbofuran, Chlorpyrifos, Oxadiazon, Ethoprophos, Dimpylate, Iso-Octyl-MCPA, Methyl dichlorofop, Endosulfan I and II, and other unknown derivatives. Anticorrosive reagents such as 1-chlorododecane and 1-chlorotetradecane and plasticizers are also significant compounds in these samples. The occurrence of pesticide and herbicide residues in most of the samples from the city is due to activities related to agriculture. Local agriculture and gardening applications of these pesticides are suggested to be the main sources of these compounds in soil and sand dust of the city. The presence of chloro-n-alkanes is attributed to contamination from antiabrasion-antiwear lubricating oils used for protecting petroleum production equipment. The occurrence of plasticizers in these samples is attributed to tyre and plastics abrasion products. n-Alkanes, UCM and series of hopane and sterane biomarkers were also detected in these samples. The n-alkanes, ranging from C_{16} to C_{36}, maximum abundances at various carbon numbers, hopane biomarkers and UCMs support the input of particles from vehicle emissions and the excess n-alkanes with odd carbon number preferences, as well as methyl n-alkanoates indicate natural vegetation sources.

Keywords: Pesticides, Herbicides, Organic contents, GC-MS, Chlor-n-alkanes, Plasticizers, n-Alkanes, UCM.

المستخلص: يعتبر الغبار العالق من التربة والرمل أحد مصادر التلوث في الجو في المناطق الجافة. وبما أن المبيدات الحشرية والنباتية أحد مكونات التلوث في تربة المناطق الزراعية، قام هذا البحث بدراسة وجود هذه المبيدات في غبار التربة والرمل من مناطق مختلفة في مدينة الرياض - المملكة العربية السعودية. هذه المبيدات بالإضافة إلى المركبات العضوية الأخرى وتشمل المحروقات الوقودية ومركبات عضوية طبيعية تم غليها بواسطة جهاز الغاز الكروموتوغرافي مع مقياس طيف الكتلة لمعرفة مصادرها وتميتها. برهنت نتائج التحليل أن أنراع مختلفة من المبيدات موجودة في غبار تربة ورمل مدينة الرياض. وتضم Chlorpyrifosc Carbfuran, Iso-octyl-MCPA, Dimpylate, Ethoprophos, Oxadiazon, Endosulfanit II, Methyldichlorofop , ومشتقاتها. كما تم التعرف على مركبات عضوية تستخدم في صناعة المركبات البترولية وكذا مركبات أخرى بلاستيكية.

كلمات مدخلية: مبيدات، ليبيدات، مركبات بلاستيكية هوبينات، سينريات.

Introduction

Anthropogenic organic matters including pesticides and herbicides are now firmly established as major carbonaceous components in the ecosphere. Their occurrence is related to human activities mainly in urban and rural areas, but also remote regions (Al-Mutlaq, *et al.* 2002; Beak, *et al.* 1991; Buehler, *et al.* 2001; Cox, *et al.* 1982; Fraser, *et al.* 1997; 1998a, b; Menichini, 1992; Rogge, *et al.* 1993a, b; 1996; Simoneit, 1986; 1989; Simoneit and Mazurek, 1989; Simoneit, *et al.* 1988; 1990; 1991a, b, c; 1993). Pesticides and herbicides, consisting of a great variety of synthetic organic compounds, have received attention because some can cause health effects (Beak, *et al.* 1991; Menichini, 1992). Much of the research to date on these compounds has been guided by the mutagenic and genotoxic potential of related compound classes found in soil, water and food (e.g., polycyclic aromatic hydrocarbon (PAH), oxygenated PAH (oxy-PAH), and nitroarenes) (Alsberg, *et al.* 1985; Choudhury, 1982; Schuetzle and Daisey, 1990; Schuetzle, *et al.* 1985; Stenberg, *et al.* 1983; Westerholm, *et al.* 1988; 1991). Some pesticide and herbicide compounds may be relatively stable molecules and

could be used to trace and quantify their presence in different environmental spheres. The characterization of anthropogenic pesticide residues and PAH may serve to further define the spatial variation and geographical sources of organic compound burdens in urban versus rural areas (Simoneit, 1984a, b; 1989).

Assessing the contribution of soil and sand resuspension into the atmosphere is a fundamental need for environmentalists and policy makers due to potential public health problems. Thus, identification and quantitation of pesticide and herbicide residues and other organic tracers for sources in soil and sand dust are essential for environmental assessments. The city of Riyadh is a typical urban location in the Arabian Peninsula to assess pesticide and herbicide residues and other organic matter because it receives input from local sources and long range atmospheric dust transport. It was selected to represent other cities in the Kingdom, where human and agricultural activities are dominant (Al-Mutlaq, *et al.* 2002). The characterization of these compounds in soil and sand dust with respect to their natural and anthropogenic sources will facilitate an understanding of their local and regional impacts. Thus, the main purpose of this study is to investigate the occurrence of pesticide and herbicide residues in soil and sand samples from the city of Riyadh, Kingdom of Saudi Arabia.

Experimental Methods

Sampling and Extraction Procedure

Outer surface layers of soil and sand samples were collected from various locations inside and outside the city of Riyadh in the Kingdom of Saudi Arabia to determine their pesticide and herbicide residues by gas chromatography-mass spectrometry (GC-MS) analysis. The samples were collected by scrapping the uppermost layers of soil and sand, where resuspension of dust and fine particles takes place. The locations and descriptions of the collected samples are shown in Figure 1 and Table 1. Duplicate samples were collected from the following locations in the winter season of 2002:

Outside the city (OC),

City center (CC),

Two market places:

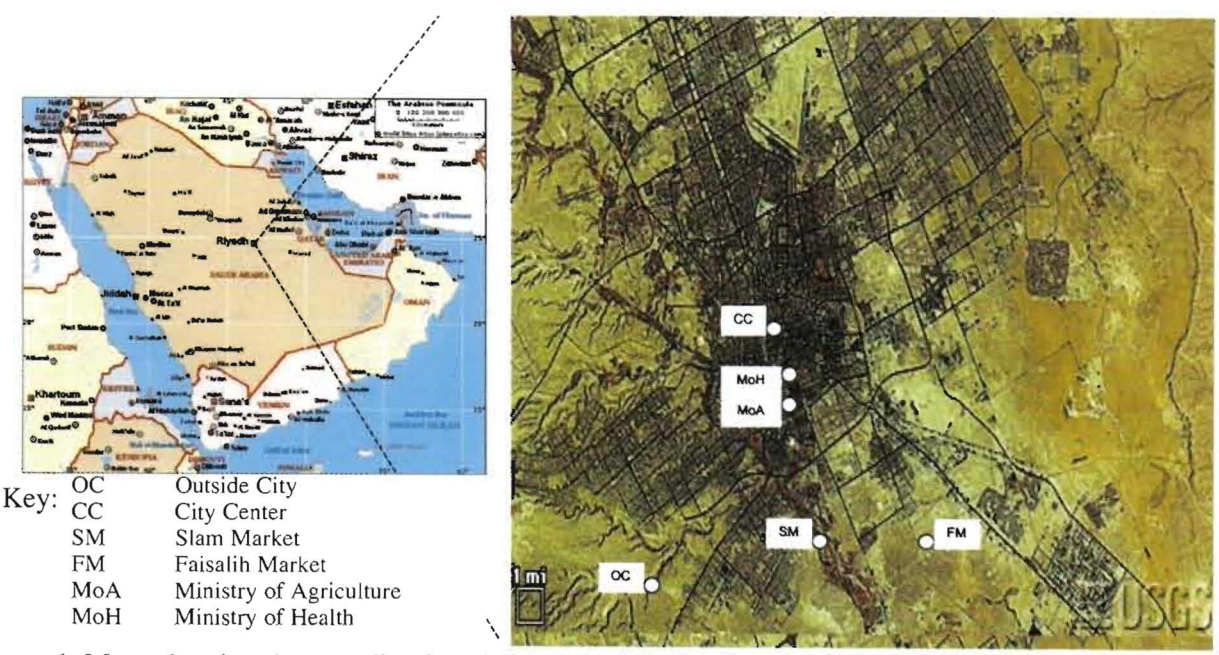
Slam market place (SM)

Faisalih market place (FM)],

The Ministry of Agriculture area (MoA),

The Ministry of Health area (MoH).

All samples were mixtures of soil and sand, except one was mostly soil (OC). Each sample was sieved to obtain fine particles (<125μm) before organic matter extraction. The extraction was performed twice by adding a mixture of methylene chloride/methanol (3:1v/v) to the sieved fine particles of each soil/sand sample and ultrasonicating for 20 minutes. Each combined extract was filtered, concentrated by evaporation, and finally under nitrogen blow-down and room temperature to approximately 50μL before GC-MS analysis.



Key:

OC	Outside City
CC	City Center
SM	Slam Market
FM	Faisalih Market
MoA	Ministry of Agriculture
MoH	Ministry of Health

Figure 1. Maps showing the sampling locations of sand and soil dust.

Table 1. Locations and descriptions of soil and sand samples collected in November 2001 from Riyadh City, Saudi Arabia.

Sample	Location	Description
Outside City	Outside the city, from palm tree farm	Mostly soil
City Center	City center	Mixture of soil and sand
Slam Market	Slam market place in the city	Mixture of soil and sand
Faisalih Market	Faisalih market place in the city	Mixture of soil and sand
Ministry of Agriculture	Ministry of Agriculture locale, in the city	Mixture of soil and sand
Ministry of Health	Ministry of Health locale, in the city	Mixture of soil and sand

Instrumental Analysis

The analysis of the total extracts was carried out by GC-MS, using a Hewlett-Packard 6890 GC coupled to a 5973 Mass Selective Detector with a DB-5MS (Agilent) fused silica capillary column (30m x 0.25mm 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 70eV ion source energy.

Mass spectrometric data were acquired and processed using the GC-MS ChemStation data system. 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-MS peak areas.

Results

The results of the organic chemical analyses indicated that all extracts consist of mixtures of organic compounds. Pesticide and herbicide residues were the major compounds in the total extracts from the market places SM and FM, and the MoA area as shown in Table 2. These pesticides and herbicides included Carbofuran, Ethoprophos, Dimpylate, Chlorpyrifos, Oxadiazon, Iso-Octyl-MCPA, Methyl dichlorofop, Endosulfan I and II, and other unknown derivatives as shown in Figures 2 and 3. The concentrations of pesticides and herbicides ranged between 0.76 and 24.4ng/g of sample. Plasticizers were also major compounds in these samples (Table 2 and Fig. 2). They were mainly diethyl phthalate, dibutyl phthalate, and dioctyl phthalate, with concentrations ranging from 0.06 to 14.90ng/g sample.

Table 2. The concentrations of major pesticide/herbicide, chloro-n-alkanes and plasticizer compounds detected in soil and sand samples from Riyadh.

Compound	Composition	MW	Concentration (ng.g^{-1} sample)					
			OC	CC	SM	FM	MoA	MoH
Pesticide/Herbicide								
Carbofuran	$C_{12}H_{15}NO_3$	221	-	-	0.18	-	-	-
Ethoprophos	$C_8H_{19}O_2PS_2$	242	-	-	-	1.64	-	-
Dimpylate	$C_{12}H_{21}N_2O_3PS$	304	-	-	0.26	-	-	-
Iso-Octyl-MCPA	$C_{17}H_{25}ClO_3$	312	-	-	-	0.28	-	-
Methyl dichlorofop	$C_{16}H_{14}Cl_2O_4$	340	-	-	-	5.26	-	-
Ronstar (Oxadiazon)	$C_{15}H_{18}Cl_2N_2O_3$	344						
Chlorpyrifos	$C_9H_{11}Cl_3NO_3PS$	349			0.31			
Endosulfan I	$C_9H_6Cl_6O_3S$	404	-	-	-	-	1.40	-
Endosulfan II	$C_9H_6Cl_6O_3S$	404	-	-	-	-	0.86	-
Total			-	-	0.75	7.18	2.26	-
Chloro-n-alkanes								
1-Chlorododecane	$C_{12}H_{25}Cl$	204	-	0.32	0.08	0.04	T	0.30
1-Chlorotetradecane	$C_{14}H_{29}Cl$	232	-	0.14	0.08	0.02	T	0.22
Total		-		0.46	0.16	0.06	T	0.52
Plasticizers								
Diethyl phthalate	$C_{12}H_{14}O_4$	222	-	-	0.06	-	-	-
Dibutyl phthalate	$C_{16}H_{22}O_4$	278	0.02	0.26	0.86	0.60	1.76	0.98
Dioctyl phthalate	$C_{24}H_{38}O_4$	390	0.04	1.74	13.98	2.90	2.38	1.22
Total			0.06	2.00	14.90	3.50	4.14	2.20
Unknown compounds			12.10	-	-	6.42	-	2.60

n-Alkanes were detected in these samples and ranged from C_{16} to C_{36}, with a maximum abundance at different carbon numbers (Figs. 2a-f). Series of hopane biomarkers were also detected and ranged from C_{27} to C_{35}, and sterane biomarkers were observed in trace amounts (Table 3). The UCM (unresolved complex mixture of branched and cyclic hydrocarbons) was obvious in these samples as illustrated in Figure 2. 1-Chlorododecane and 1-chlorotetradecane were also detected (Table 2, Fig. 3). Methyl n-alkanoates were found in all samples from the Riyadh area and ranged from C_{13} to C_{29} (Table 3). A major amount of unknown pesticide residues was found in the FM sample (Figures 2d and 3j and Table 2).

Table 3. Carbon number range and maximum of various organic compound groups in total extracts of soil and sand samples from outside and in Riyadh.

Compound Class	Sample Code					
	OC	CC	SM	FM	MoA	MoH
n-Alkanes						
Range	18-36	16-37	16-35	16-35	16-35	16-35
C_{max}	29	29	27	20	21	29
CPI	3.6	1.4	1.1	1.1	1.1	3.5
Methyl n-alkanoates						
Range	16-29	13-25	13-19	13-19	13-29	13-29
C_{max}	17	17	17	17	17	17
Hopane Biomarkers						
Range	-	27-34	27-35	27-33	29-30	27-35
C_{max}	-	29	29	29	29,30	29
Sterane Biomarkers						
Range	27-29	27-29	-	27-28	27-29	27-29
C_{max}	29	29	-	29	29	29

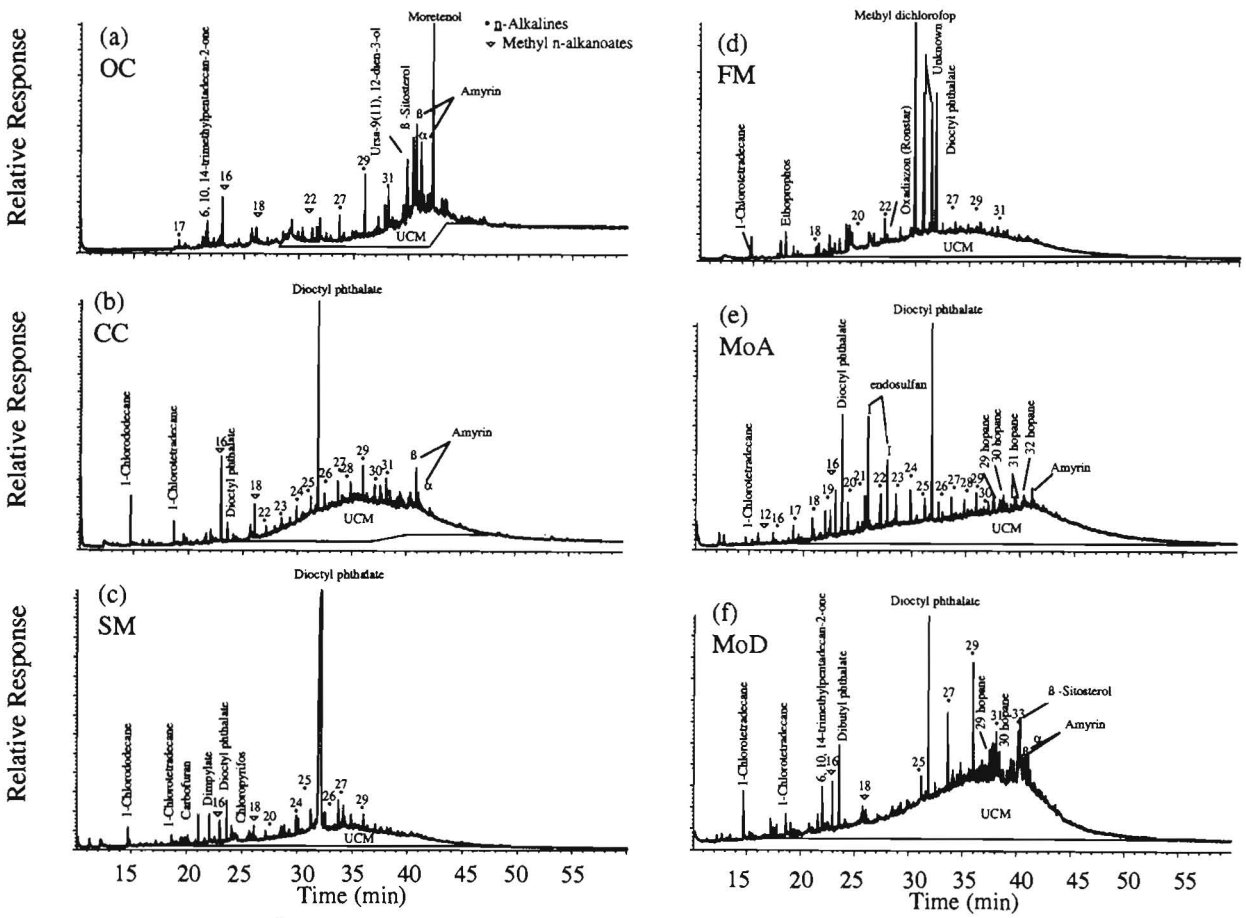


Figure 2. GC-MS total ion current traces of total extracts from soil and sand samples of Riyadh showing the major organic components: a) Outside the city (OC); b) City center (CC); c) Slam market place (SM); d) Faisalih market place (FM); e) Ministry of Agriculture area (MoA); and f) Ministry of Health area (MoH).

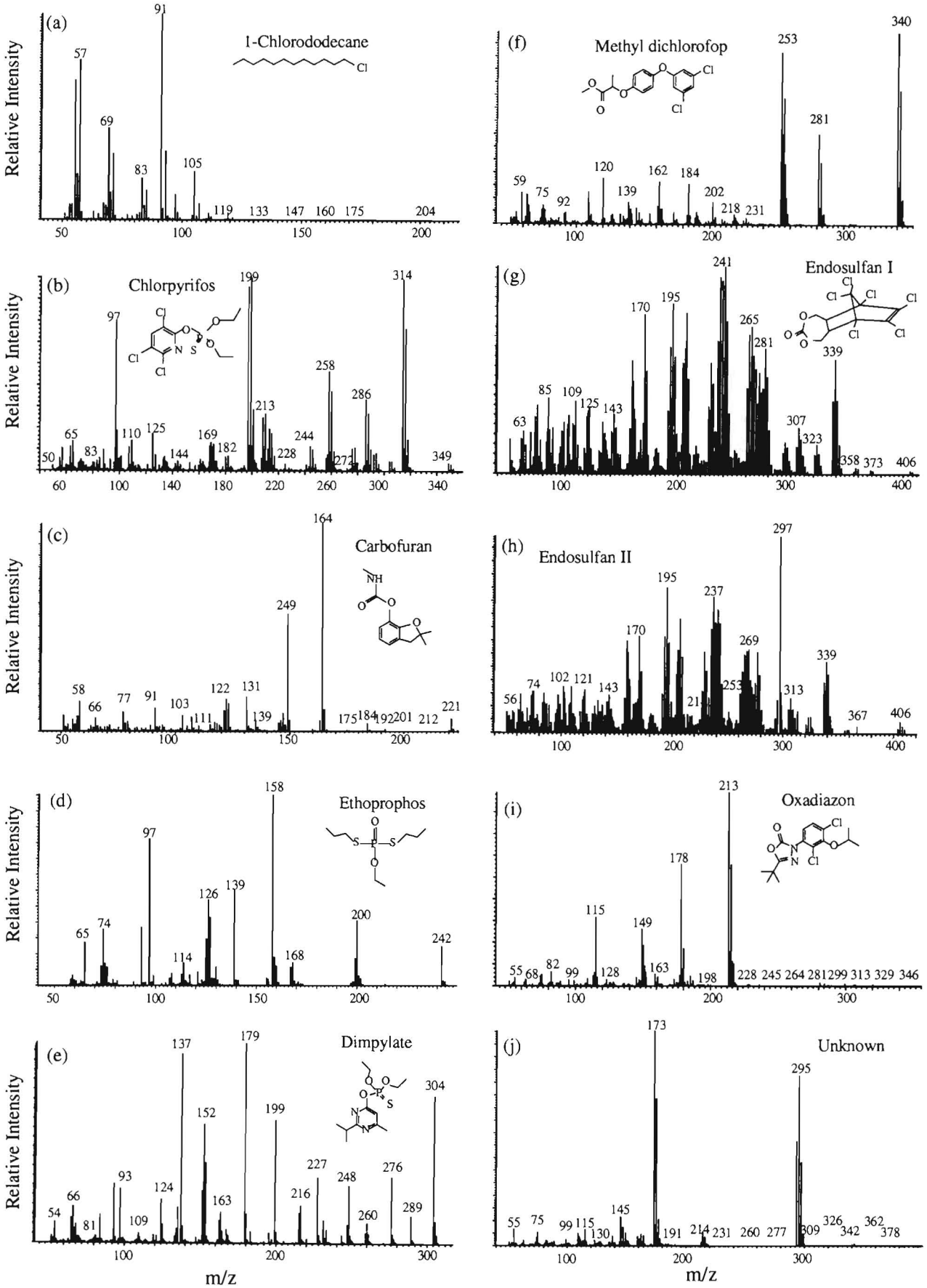


Figure 3. Mass spectra of chloro-n-alkanes, pesticides and herbicides detected in the soil and sand samples from Riyadh: a) 1-Chlorododecane; b) Chlorpyrifos; c) Carbofuran; d) Ethoprophos; e) Dimpylate; f) Methyl dichlorofop; g) Endosulfan I; h) Endosulfan II; i) Oxadiazon (Ronstar); and j) unknown.

Discussion

The data of the organic chemical analysis of the soil and sand dust from the Riyadh area indicate that anthropogenic sources from urban and agriculture related activities are significant. Natural background sources from local and external vegetation are a minor input of organic components.

Pesticide and Herbicide Residues

These results indicate that market places in the city of Riyadh are major sources of anthropogenic organic compounds, such as pesticide and herbicide residues and plasticizers. They are major components in dust samples collected around market places where pesticide and herbicide stores conduct business. This suggests that these local stores are the main sources of these compounds in the urban soil and sand dust. Spills of these pesticides and herbicides near and around these stores are expected to occur. This is supported by the occurrence of these compounds mainly in the samples from Slam market place, Faisalih market place, and the Ministry of Agriculture area and their absence in the other samples. Furthermore, each sample from each market place contains specific classes of pesticide and herbicide residues, indicating that each market place and probably each store sells a specific type or group of pesticide and herbicide. Other sources and atmospheric transport of these compounds by dust to these sites in the city are unlikely. The detection of plasticizers in soil and sand dust from the city is attributed to contamination from plastic bags used by shops and stores of these local markets and other urban uses of plastics.

The toxicity of compounds such as Ethoprophos, Carbofuran, and Endosulfan varies. They are registered as hazardous materials and their effects range from acute to chronic human health effects (Battaglin, *et al.* 2001; Khare, *et al.* 2002). For instance Endosulfan, which has been detected in breast milk (Sanghi, *et al.* 2003), can reduce the oxygen uptake in blood (Bhalchandra and Lomte, 2003).

Urban Traffic Emissions

The presence of n-alkanes, UCM, hopanes and traces of steranes (Table 3, Fig. 2) indicate anthropogenic sources from vehicle emissions (Simoneit, 1984a, b). The increase of even carbon numbered n-alkanes in the samples from inside the city indicates an input of n-alkanes from combustion emissions of fossil fuel (petroleum). This is evident in the decrease of the carbon preference index (CPI, o/e) from 3.6 to 1.0 (Table 3). The UCM, which is the major petroleum component derived from lubricating oil in vehicle exhaust (Simoneit, 1984a, b), further supports the contribution from traffic emissions (Fig. 2). The presence of biomarker hopanes and steranes in the samples confirms the contribution from urban traffic (Simoneit, 1984a, b). These petroleum biomarker compounds are found at highest concentrations in samples from the city center, market places and the Ministries of Agriculture and Health areas. The absence of major PAH compounds indicates that burning processes (e.g., biomass) are not a major source of organic matter in these samples (Simoneit, 2002). The occurrence of 1-chlorododecane and 1-chlorotetradecane is due to contamination from inhibitor products used as protection of equipment for petroleum recovery (Lee and Lim, 2000; Shakhovtseva, *et al.* 2000).

Natural Background

The n-alkanes with odd carbon number predominances, homolog maxima at C_{27}, C_{29} and/or C_{31} and CPI(o/e) >3 are dominant in samples from outside the city and the Ministry of Health area (see Fig. 2). This indicates that natural background wax from vegetation is the main source of aliphatic compounds in these samples (Simoneit, 1977a, b; 1989). The presence of terpenoids (e.g., amyrins and moretenol from higher vascular plants, Brassell, *et al.* 1983; Simoneit, 1989), methyl n-alkanoates (from plant biomass, Holloway, 1982) and phytosterols (e.g., (ßsitosterol from vegetation, Barbier, *et al.* 1981; Simoneit, *et al.* 1983) also indicate natural background sources (Table 3 and Fig. 2). Organic detritus from vegetation is obviously abundant in the samples from outside the city and the area of the Ministry of Health in Riyadh.

Conclusion

The organic chemical analyses of total solvent extracts from soil and sand dust samples collected from the city of Riyadh indicated that anthropogenic inputs are the major sources of the organic compounds. These anthropogenic inputs are mainly from agriculture related activities and urban traffic emissions. The agriculture related compounds include pesticide and herbicide residues from stores,

plasticizers from plastic bags and other plastics used by local commerce and petroleum related compounds from vehicle emissions and lubricants. Natural background organic matter from local and regional vegetation sources is minor relative to the anthropogenic compounds in the samples from the city.

The greater contribution of anthropogenic versus natural organic components is significant and requires further studies to determine the fraction of each source of organic components to soil and sand dust in Riyadh. Additional detailed studies are also needed to identify the reason(s) for the occurrence and distribution of these pesticides and herbicides in certain locations and not in others. Resuspension and redistribution of soil and sand dust particles by wind contributes to the total fine particle burden in an urban atmospheric environment and thus to inhalation by the population. Therefore, hazardous organic compounds in dust may contribute to public health problems in such urban areas. The characterization, identification and quantification of organic compounds in soil, sand and atmospheric particulate matter of remote versus rural areas are also crucial and important in order to facilitate the processes of environmental assessment and prediction of the impact of these compounds on human health.

References

Al-Mutlaq, K, Rushdi, AI and Simoneit, BRT (2002) Characteristics and sources of organic matter in desert sand samples from the Riyadh and Al-Qasim areas of Saudi Arabia: Preliminary results. Arab Gulf J of Scientific Research **20**:141-155.

Alsberg, T, *et al*, (1985) Chemical and biological characterization of organic material from gasoline exhaust particles. Environmental Science and Technology **19**:43-50.

Barbier, M, Tusseau, D, Marty, JC and Saliot, A (1981) Sterols in aerosols, surface microlayer and subsurface water in the North-Eastern tropical Atlantic. Oceanologica Acta **4**: 77-84.

Battaglin, WA, Furlong, ET, and Brukhardt, MR (2001) Water-Resources Investigations Report 00-4225, U.S. Geological Survey, Denver, Colorado, USA.

Beak, SO, *et al* (1991) A review of atmospheric polycyclic aromatic hydrocarbons: Fate and behavior. Water, Air, Soil Pollution **60**: 279-300.

Bhalchandra, W and Lomte, VS (2003) Respiratory response of fresh water bivalve, Parreysia cylindrica to endosulfan. Pollution Research **22**: 125-128.

Brassell SC, Eglinton G and Maxwell JR (1983) The geochemistry of terpenoids and steroids. Biochemical Society Transactions **11**: 575-586.

Buehler, S, Bsua, I and Hites, RA (2001) A comparison of PAH, PCB, and pesticide concentrations in air at two rural sites on Lake Superior. Environmental Science and Technology **35**: 2417-2422.

Choudhury, DR (1982) Characterization of polycyclic ketones and quinones in diesel emission particulates by gas chromatography/mass spectrometry. Environmental Science and Technology **16**: 102-106.

Cox, RE, Mazurek, MA and Simoneit, BRT (1982) Lipids in Harmattan aerosols of Nigeria. Nature. **296**: 848-849.

Fraser, MP, Cass, GR, Simoneit, BRT and Rasmussen, RA (1997) Air quality model evaluation data for organics. 4 C_2-C_{36} non-aromatic hydrocarbons. Environmental Science and Technology **31**: 2356.

Fraser, MP, Cass, GR, Simoneit, BRT and Rasmussen, RA (1998a) Air quality model evaluation data for organics. 5. C_6-C_{22} nonpolar and semipolar aromatic compounds. Environmental Science and Technology **32**: 1760-1770.

Fraser, MP, Cass, GR and Simoneit, BRT (1998b) Gas-phase and particle-phase organic compounds emitted from motor vehicle traffic in a Los Angeles roadway tunnel. Environmental Science and Technology **32**: 2051-2060.

Holloway, PJ (1982) The chemical contribution of plant cutins. *In: Cutler, D. F., Alvin, K. L. and Price, C. E. (eds.)* The Plant Cuticle. Linnean Soc., Academic Press, London, pp. 45-85.

Khare, S, Singh, S and Mehrotra, A (2002) Histopathological changes in the gills of *Nandus nandus* induced by endosulfan and carbaryl. Nature, Environment and Pollution Technology **1**: 1-4.

Lee, HJ and Lim, YH (2000) Antiabrasion-antiwear lubricating oils for thick-film, extreme-pressure, and boundary lubrication regimes. (Patent written in Korean.)

Menichini, E (1992) Urban air pollution by polycyclic aromatic hydrocarbons: levels and sources of variability. Science of Total Environment **116**: 109-135.

Rogge, WF, *et al* (1993a) Sources of fine organic aerosol: 2. Noncatalyst and catalyst-equipped automobiles and heavy-duty diesel trucks. Environmental Science and Technology **27**: 636-651.

Rogge, WF, *et al* (1993b) Quantification of organic aerosols on a molecular level: Identification, abundance and seasonal variation. Proc. Fourth Int. Conf. on Carbonaceous Particles in the Atmosphere. Atmospheric Environment **27A**: 1309-1330.

Rogge, WF, *et al* (1996) Mathematical modeling of atmospheric fine particle-associated primary organic compound concentrations. J of Geophysical Research **101**(D14): 19379-19394.

Sanghi, R, Pillai, MKK, Jayalekshmi, TR and Nair, A (2003) Organochlorine and organophosphorous pesticide residues in breast milk from Bhopal, Madhya Pradesh, India. Human and Experimental Toxicology **22**: 73-76.

Schuetzle, D and Daisey, JM (1990) Identification of genotoxic agents in complex mixtures of air pollutants. Environmental Science Research **39**: 11-32.

Schuetzle, D, Jensen, TE and Ball, JC (1985) Polar polynuclear aromatic hydrocarbon derivatives in extracts of particulates: biological characterization and techniques for chemical analysis. Environmental International **11**: 169-181.

Shakhovtseva, GA, *et al* (2000) A method for preparation of salt corrosion inhibitor. Patent written in Russian.

Simoneit, BRT (1977a) Organic matter in eolian dust over the Atlantic Ocean. Marine Chemistry **5**: 443-464.

Simoneit, BRT (1977b) Diterpenoid compounds and other lipids in deep-sea sediments and their geochemical significance. Geochimica et Cosmochimica Acta **41**: 463-476.

Simoneit, BRT (1984a) Organic matter of the troposphere - III. Characterization and sources of petroleum and pyrogenic residues in aerosols over the western United States. Atmoshperic Environment **18**: 51-67.

Simoneit BRT (1984b) Application of molecular marker analysis to reconcile sources of carbonaceous particulates in tropospheric aerosols. Science of the Total Environment **36**: 61-72.

Simoneit, BRT (1986) Characterization of organic constituents in aerosols in relation to their origin and transport: A review. International J of Environmental Analytical Chemistry **23**: 207-237.

Simoneit, BRT (1989) Organic matter of troposphere - V: Application of molecular marker analysis to biogenic emissions into the troposphere for source reconciliations. J of Atmospheric Chemistry **8**: 251-275.

Simoneit, BRT (2002) Biomass burning- A review of organic tracers in smoke from incomplete combustion. Applied Geochemistry 17: 129-162.

Simoneit, BRT, and Mazurek, MA (1989) Organic tracers in ambient aerosols and rain. Aerosol Science and Technology **10**: 267-291.

Simoneit, BRT, Mazurek, MA and Reed, WE (1983) Characterization of organic matter in aerosols over rural sites: Phytosterols, *In: Bjor¯y, M. et al. (eds.) Advances in Organic Geochemistry 1981*. J. Wiley and Sons Ltd., Chichester, pp. 355-361.

Simoneit, BRT, Cox, RE and Standley, LJ (1988) Organic matter of the troposphere-IV: Lipids in Harmattan aerosol particles of Nigeria. Atmospheric Environment **22**: 983-1004.

Simoneit, BRT, Cardoso, JN and Robinson, N (1990) An assessment of the origin and composition of higher molecular weight organic matter in aerosols over Amazonia. Chemosphere **21**: 1285-1301.

Simoneit, BRT, Cardoso, JN and Robinson, N (1991a) An assessment of terrestrial higher molecular weight lipid compounds in air particulate matter over the South Atlantic from about 30-70°S. Chemosphere **23**: 447-465

Simoneit, BRT, *et al* (1991b) Molecular marker study of extractable organic matter in aerosols from urban areas of China. Atmospheric Environment **25A**: 2111-2129.

Simoneit, BRT, Crisp, PT, Mazurek, MA and Standley, LJ (1991c) Composition of extractable organic matter of aerosols from the Blue Mountains and southeast coast of Australia. Environment International **17**: 405-419.

Simoneit BRT., et al (1993) Lignin pyrolysis products, lignans and resin acids as specific tracers of plant classes in emissions from biomass combustion. Environmental Science and Technology **27**: 2533-2541.

Stenberg U, Alsberg T and Westerholm R (1983) Applicability of cryogradient technique for the enrichment of PAH from automobile exhausts: demonstration of methodology and evaluation experiments. Environmental Health Perspective **47**: 43-51.

Westerholm, RN, *et al* (1988) Effect of fuel polycyclic aromatic hydrocarbon content on the emissions of polycyclic aromatic hydrocarbons and other mutagenic substances from a gasoline-fueled automobile. Environmental Science and Technology **22**: 925-930.

Westerholm, RN, *et al* (1991) Chemical and biological characterization of particulate-, semivolatile-, and gas-phase-associated compounds in diluted heavy duty diesel exhaust: A comparison of three different semivolatile-phase samplers. Environmental Science and Technology **25**: 332-338.

Received 02/05/2004, in revised form 13/072004