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5 **Occurrence and sources of natural and anthropogenic**
6 **lipid tracers in surface soils from arid urban areas of**
7 **Saudi Arabia**
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ABSTRACT

44 Soil particles contain a variety of natural and anthropogenic organic components,
45 and in urban areas can be considered as local collectors of pollutants. Surface soil
46 samples were taken from ten urban areas in Riyadh during early winter of 2007. They
47 were extracted with dichloromethane-methanol mixture and the extracts were analyzed
48 by gas chromatography-mass spectrometry. The major compounds were unresolved
49 complex mixture (UCM), plasticizers, n-alkanes, carbohydrates, n-alkanoic acids,
50 hopanes, n-alkanols, and sterols. Vegetation detritus was the major natural source of
51 organic compounds ($24.0 \pm 15.7\%$) in samples from areas with less human activities and
52 included n-alkanes, n-alkanoic acids, n-alkanols, sterols and carbohydrates. Vehicular
53 emission products and discarded plastics were the major anthropogenic sources in the soil
54 particles ($53.3 \pm 21.3\%$ and $22.7 \pm 10.7\%$, respectively). The anthropogenic tracers were
55 UCM, plasticizers, n-alkanes, hopanes and traces of steranes. Vegetation and human
56 activities control the occurrence and distribution of natural and anthropogenic extractable
57 organic matter in this arid urban area.

58

Capsule:

60 This work shows that human activities are critical factors that influence the
61 characteristics and distribution of EOM in soils of arid urban regions.

62

63 **Key words:** soils, biomarkers, lipids, petroleum residues, plasticizers.

64

65 **1. Introduction**

66 Biogenic and anthropogenic organic matter (OM) is a major carbonaceous
67 fraction in different ecosystems (e.g. [Hansell and Carlson, 2014](#); [Lischke et al., 2014](#);
68 [Schmidt et al., 2011](#)). The occurrence and concentrations of OM in urban and
69 rural/remote region soils vary spatially and seasonally ([Fraser et al., 1998](#); [Kononova,](#)
70 [2013](#); [Oros et al., 2002](#); [Trendel et al., 2010](#)). One of the primary sources of OM in soil is
71 material from plant litter. Other sources include anthropogenic organic chemicals such as
72 pesticides and fossil fuel residues from vehicles ([Al-Mutlaq et al., 2005, 2007](#); [Rushdi et](#)
73 [al., 2005, 2013](#); [Yang et al., 2013](#)). The composition, properties and distribution of this
74 OM controls the formation of soil organic matter (SOM) and humification processes
75 ([Kononova, 2013](#); [Scholes et al., 1997](#); [Schmidt et al., 2011](#)). Microbial activity and
76 biomass are also important factors in SOM formation and alteration ([Schmidt et al.,](#)
77 [2011](#)). Therefore, SOM varies in composition and properties. The major studies on soil
78 OM have focused on bulk properties ([Kögel-Knabner, 2000](#); [Martin and Haider, 1986](#)),
79 whereas extractable organic matter (lipid) studies are relatively few ([Otto and Simpson,](#)
80 [2005](#); [Rogge et al., 2012](#); [Rushdi et al., 2005, 2006](#)). Less attention has been paid to the
81 lower molecular weight OM ([Kögel-Knabner, 2000](#)).

82 Lipid compounds usually comprise 1-5% of the total SOM. They are derived from
83 plants, fungi, bacteria and mesofauna, and generally consist of n-alkanes, n-alkanols, wax
84 esters, fatty acids, steroids, terpenoids and acyl glycerols ([Oros et al., 2002](#)). These
85 products are a result of decomposition and exudation of OM from various sources ([Miller](#)
86 [and Donahue, 1995](#)). Lipids can be found either free in the soil matrix, chemically bound

87 in humic and fulvic material, or absorbed to soil particles ([Kononova, 2013](#); [Schmidt et](#)
88 [al., 2011](#)).

89 Thus, characterization and identification of organic compounds and OM contents
90 of surface soils are important for understanding the OM composition and compound
91 sources that may be introduced to the different environmental compartments, such as for
92 example: (1) absorption into the food chain, (2) advection into the atmosphere via dust
93 resuspension, machinery and/or human activities, and (3) wash-in to water reservoirs. It
94 will also aid to better understand the various effects on human health and environmental
95 assessment processes.

96 The extractable organic matter (EOM) of surface soil has not been fully
97 characterized for the Arabian Peninsula region. The preliminary results have shown that
98 soil and sand dusts from Kuwait and Saudi Arabia contained a mixture of natural and
99 anthropogenic OM ([Al-Mutlaq et al., 2002, 2007](#); [Rushdi et al., 2005, 2006](#)). Based on
100 aliphatic hydrocarbon contents of soil from Riyadh, the natural and anthropogenic
101 sources ranged from 20 to 57% and from 30 to 55% of the total lipid tracers, respectively
102 ([Rushdi et al., 2005](#)). Soil and sand samples from the vicinity of Kuwait City showed that
103 the natural sources ranged from 15 to 78% and the anthropogenic sources ranged from 8
104 to 88% of the total lipid compounds ([Rushdi et al., 2006](#)).

105 The research hypotheses of this work are: (1) the EOM sources in soils of an
106 urban arid region is mainly from traffic emissions; and (2) the sources of natural EOM
107 are relatively low and are primarily from soil microbiota with lesser contributions from
108 vegetation. Therefore, the main objectives of this work are to: (1) determine the chemical
109 composition of the solvent EOM in soils from arid urban areas in Saudi Arabia, (2)
110 identify the main sources of the EOM, and (3) examine the relative changes in the source

111 abundances of the EOM. Consequently, surface soil samples were collected from various
112 locations such as public parks, streets, and agricultural fields in the city of Riyadh to
113 investigate the occurrence of natural biogenic and anthropogenic lipid compounds.

114

115 **2. Experimental Methods**

116 *2.1. Sampling and Extraction Procedure*

117 Surface oil samples were collected in November 2007 from different metropolitan
118 areas of the city of Riyadh in Saudi Arabia to characterize their solvent extractable lipid
119 contents by gas chromatography-mass spectrometry (GC-MS) analysis. The samples
120 were taken by scraping the uppermost layer (~1cm) of the soil in a 30 cm² area of
121 exposed surface. The locations of the samples were chosen to represent urban areas in
122 and around Riyadh, ranging from highly populated, with different human activities such
123 as public markets (OL), governmental site (NZ), industrial area (MN), rural areas with
124 limited human impact (OG), and areas with agriculture (AQ, JZ, DR) (Fig. 1).

125 After air drying, each sample was sieved to obtain the fine particles (<125µm)
126 before extraction. The extraction was performed twice by adding a mixture of
127 dichloromethane/methanol (40 mL 3:1 v/v) to about 5 g of the particles of each sample,
128 ultra-sonicating for 20 min, and then filtering through pre-extracted glass microfiber
129 filters (*Whatman*[®], GF/A filters). Each total extract was concentrated under nitrogen
130 blow-down at room temperature to approximately 1.0-1.5 mL before GC-MS analysis. A
131 50 µL aliquot of each total extract was also derivatized with silylating reagent [N,O-
132 bis(trimethylsilyl)trifluoroacetamide, BSTFA, *Pierce Chemical Co*] by the standard
133 procedure before analysis by GC-MS. This derivatizing agent replaces the H in hydroxyl

134 groups with a trimethylsilyl [(CH₃)₃Si, i.e., TMS] group for better GC resolution of polar
135 compounds.

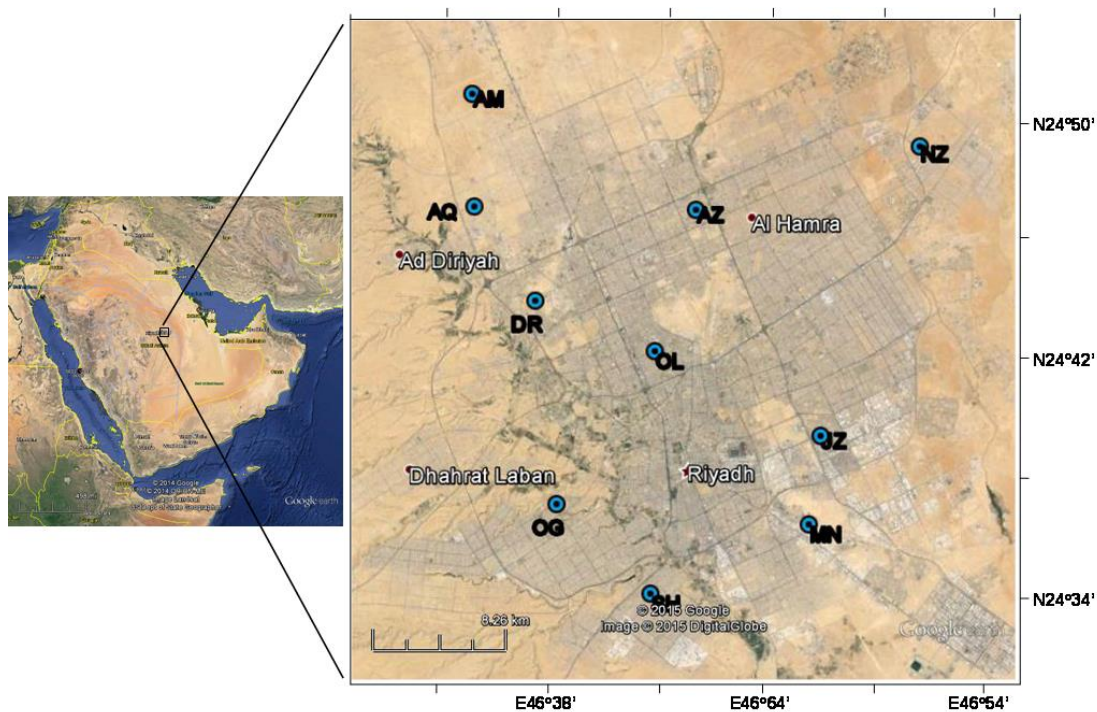


Figure 1. Map showing the sampling sites and locations of the soil samples.

136

137 2.2. Instrumental Analysis

138 The analyses of the total and silylated extracts were carried out by GC-MS, using an
139 Agilent 6890 GC coupled to a 5973 Mass Selective Detector with a DB-5 (*Agilent*) fused
140 silica capillary column (30 m x 0.25 mm i.d., 0.25µm film thickness) and helium as the
141 carrier gas. The GC was temperature programmed from 65°C (2 min initial time) to
142 300°C at 6°C min⁻¹ (isothermal for 20 min final time). The MS was operated in the
143 electron impact mode at 70 eV ion source energy. The data were acquired and processed
144 with an Agilent ChemStation.

145 Compounds were identified by GC retention index and comparison of mass
146 spectra with those of authentic standards, literature and library data, or characterized
147 mixtures. Unknown compounds were characterized by interpretation of the fragmentation
148 pattern of their mass spectra. The concentrations of the compounds in ng g^{-1} sample were
149 obtained from ratios of peak areas in the total ion current traces of the samples versus the
150 peak areas of a mixture of quantitative standards.

151

152 2.3. *Quality Control*

153 Throughout the study, emphasis has been placed on the technical accuracy of the
154 research. This applied to sample collection, analytical chemistry, biomarker tracer
155 determination, and geochemical interpretation. All solvents used in the analytical workup
156 procedure were tested for possible contaminants. Procedural blanks were analyzed to
157 provide a qualitative and quantitative assessment of background contamination
158 introduced by laboratory procedures. Blank extracts were performed through the entire
159 project with batches of three samples. *The contamination background levels were*
160 *insignificant in all procedural blanks.* The recoveries of external standards (tetracosane
161 for n-alkanes; hexadecanoic acid for n-alkanoic acids, alkyl alkanoates and n-alkanols;
162 sitosterol for triterpenoids; glucose for monosaccharides; and sucrose for disaccharides)
163 ranged from 72 to 105%.

164

165

166 **3. Results and Discussion**

167 The total extract compositions of the soil samples from the metropolitan Riyadh
168 area are given in Table SM1 (Supplementary Material) and vary in contents depending on

169 the locations and human activities. This variation is illustrated by the data for samples
 170 from the city center (Fig. 2a, sample OL) and outside the city (Fig. 2b, sample OG). The
 171 EOM consists mainly of mixtures of n-alkanes, n-alkanoic acids, sterols, n-alkanols,
 172 carbohydrates hopanes, plasticizers, and UCM (unresolved complex mixture, mainly of
 173 branched and cyclic hydrocarbons from petroleum products, Simoneit, 1985).

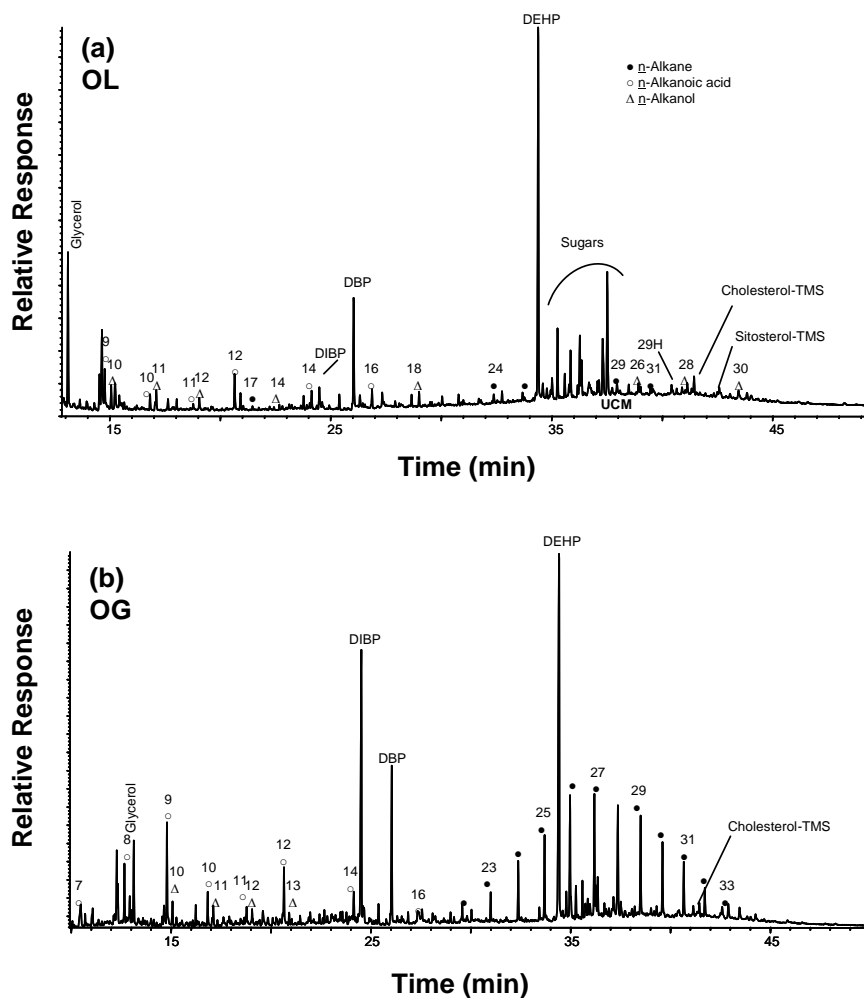


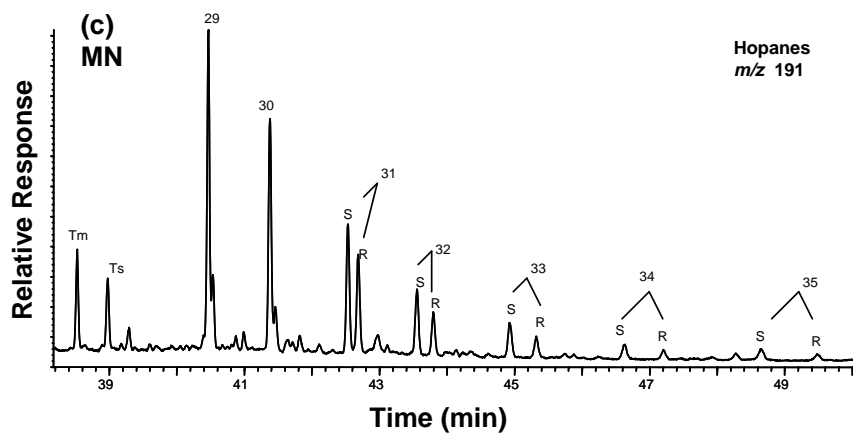
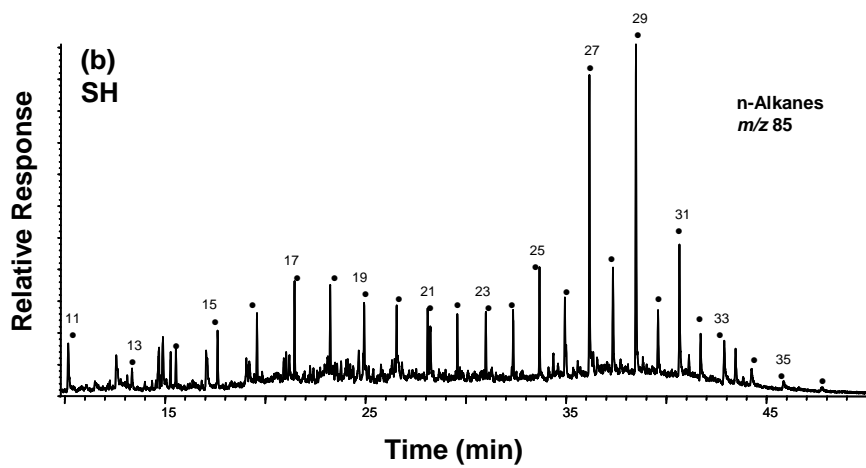
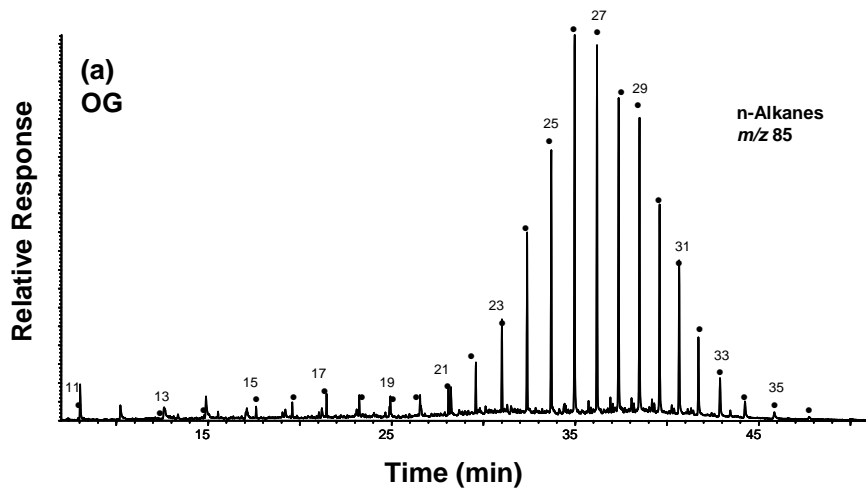
Figure 2. GC-MS total ion current traces of total extracts of the soil samples from outside and in the city of Riyadh showing the major organic components: a) OL (center); b) OR (outside the city) (Numbers refer to the carbon chain length and symbols are: DIBP= diisobutyl phthalate, DBP= dibutyl phthalate and DEHP = diethylhexyl phthalate, H = hopanes, and UCM = unresolved complex mixture).

175 The n-alkanes were detected in all samples and ranged from C₁₃ to C₃₅ with a
176 maximum concentration (C_{max}) at nonadecane, eicosane or heneicosane for some samples
177 and heptacosane, nonacosane or hentriacontane for others (Fig. 3a,b; Table SM1). The
178 concentrations of the total n-alkanes ranged from 0.10 to 4.28 µg g⁻¹ with an average
179 value of 1.64±1.53 µg g⁻¹.

180 The n-alkanoic acids ranged from C₆ to C₁₈ with a C_{max} at octanoic and nonanoic
181 acids in all samples, except sample JZ where the C_{max} was at tetradecanoic acid (Table
182 SM1). Their total concentrations ranged from 0.06 to 2.29 µg g⁻¹ with an average value of
183 0.70±0.69 µg g⁻¹. The n-alkanols were also present in all samples and ranged from C₁₀ to
184 C₃₀ with a C_{max} at tetradecanol, hexadecanol, octadecanol, octacosanol or triacontanol.
185 The total concentrations of n-alkanols ranged from 0.06 to 0.43 µg g⁻¹ with an average
186 value of 0.17±0.12 µg g⁻¹.

187 Sterols were found in all samples and included mainly cholesterol, brassicasterol,
188 campesterol, stigmasterol and sitosterol. The maximum concentration was either
189 cholesterol or sitosterol. The total concentration of sterols ranged from 0.03 to 0.35 µg g⁻¹
190 (mean = 0.12±0.11 µg g⁻¹). The carbohydrates in the soil samples included glucose,
191 sucrose and mycose as well as glycerol (sugar alcohol). The maximum concentration was
192 glucose, sucrose or mycose. The total concentrations of carbohydrates ranged from 0.18
193 to 3.22 µg g⁻¹ with an average concentration of 0.73±0.76 µg g⁻¹.

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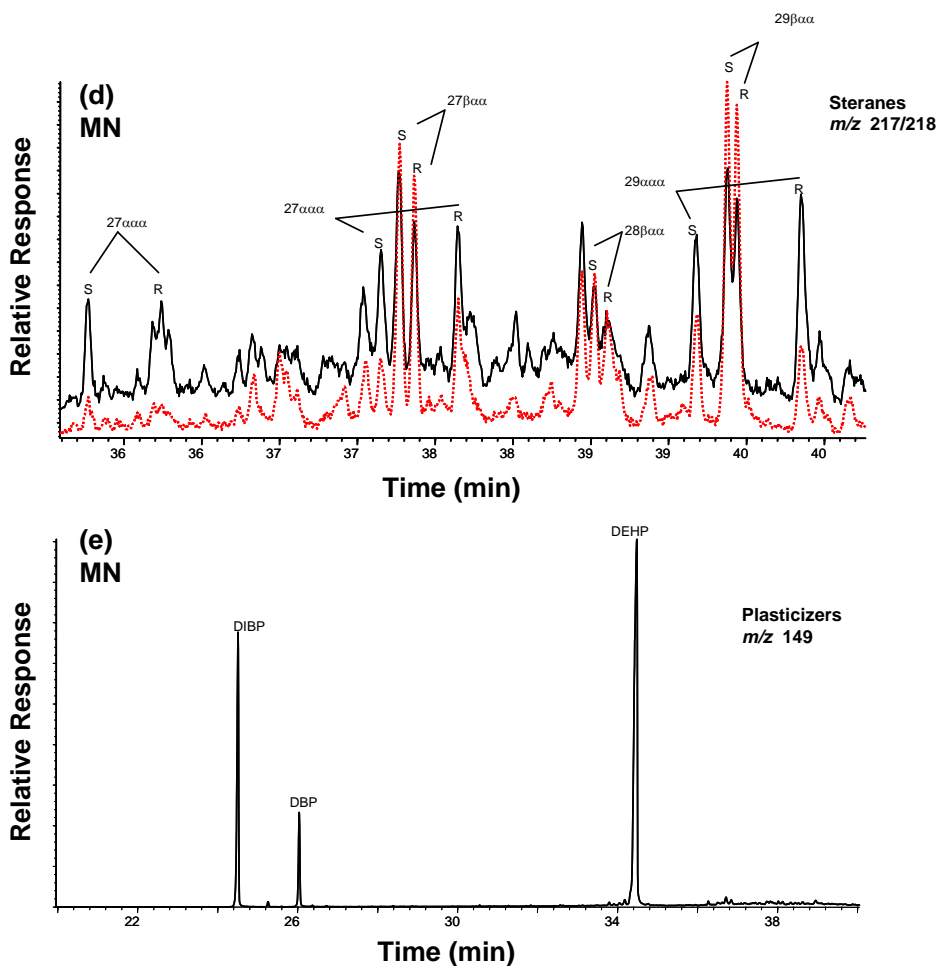


Figure 3. Examples of typical GC-MS key ion plots for various compound series found in the soil samples: a) OR and b) SH, m/z 85 for n -alkanes; c) MN, m/z 191 for hopanes; d) MN, m/z 217 and 218 for steranes, and e) MN m/z 149 for phthalate plasticizers.

196

197 Hopanes, biomarkers for petroleum residues (Peters and Moldowan, 1993;
 198 Simoneit, 1985), were found to range from C_{27} to C_{35} , with a C_{max} at 29 and 30 (e.g. Fig.
 199 3c), and concentrations from 0.02 to $3.35 \mu\text{g g}^{-1}$, mean $0.47 \pm 1.08 \mu\text{g g}^{-1}$. The C_{27} to C_{29}
 200 steranes were only detectable in the sample from Manakh (MN) at a concentration of
 201 $7.36 \mu\text{g g}^{-1}$ (Fig. 3d). Plasticizers, including diethyl-, dibutyl-, dioctyl-phthalates and
 202 dioctyl adipate, were significant components of these samples (Figs. 2 and 3e), with
 203 concentrations ranging from 0.37 to $8.03 \mu\text{g g}^{-1}$ and mean of $2.49 \pm 2.40 \mu\text{g g}^{-1}$.

204 The UCM concentrations were high in some samples and ranged from 0.0 to
205 83.28 $\mu\text{g g}^{-1}$. The average concentration of the UCM was $9.59 \pm 26.03 \mu\text{g g}^{-1}$.

206 The results indicate that both natural biogenic and anthropogenic sources are the
207 main inputs of the EOM to the soil samples of the city of Riyadh. Therefore, the entire
208 data set was statistically analyzed by principal component analysis (PCA) techniques
209 using the SPSS (IBM-Statistical Package for the Social Sciences, version 21) software to
210 understand the similarity among the different sites. The output of the PCA analysis,
211 explaining 85.1% of the variance, is shown in Figure 4a where two site groups were
212 recognized. The first group (C1 explains 47.1%) included the sites AQ, NZ, DR, OG,
213 AZ, JZ and OL; and the second one (C2 explains 25.4%) included the AM, MN and SH
214 sites. The MN site was in an industrial area and the AM and SH sites were in an area
215 where large trucks usually gather and idle before entering the city. The rest of the sites
216 were in different locations inside the city. This indicates that the locations and the type of
217 human activities have an impact on the characteristics and distributions of EOM in the
218 region.

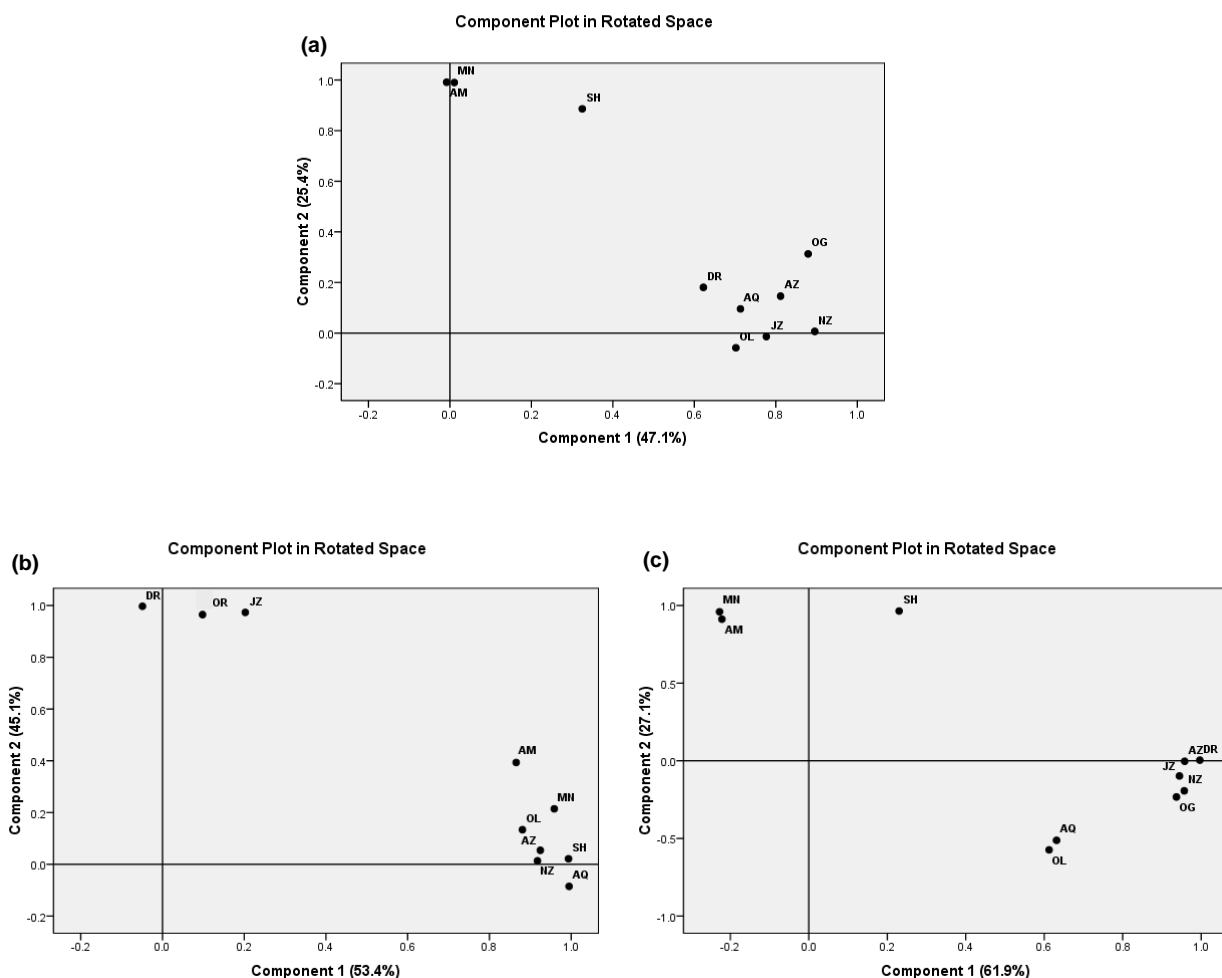


Figure 4. Plots showing the statistical outputs of principal component analysis (PCA) for: (a) entire compounds; (b) natural biogenic compounds and (c) anthropogenic compounds.

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220

221 3.1. Natural biogenic sources

222 The occurrence and distribution of vegetation wax lipids, such as n-alkanes (in
 223 part), n-alkanols, and sterols, validates the natural source input from higher plant biomass
 224 to the soils, as well as carbohydrates indicate input from plant detritus (e.g. roots) and
 225 microbial/fungal activity in the soils (Otto and Simpson, 2005; Simoneit, 2006; Trendel
 226 et al., 2010). Plant wax n-alkanes show a C_{max} in the range of 25 to 33, which depends on

227 the plant species, as well as the season and locality (e.g. [Simoneit, 1977](#); [Buch and](#)
228 [McInerney, 2013](#); [Eglinton and Hamilton, 1967](#)). A CPI (here the ratio of
229 $\sum(C_{23}+C_{25}+C_{27}+C_{29}+C_{31}+C_{33}+C_{35})$ -to- $\sum(C_{22}+C_{24}+C_{26}+C_{28}+C_{30}+C_{32}+C_{34})$ value of >1.0
230 is also an indicator of natural sources, whereas a CPI ~ 1.0 ([Table SM1](#)) supports a source
231 from fossil fuel utilization ([Bray and Evans, 1961](#); [Mazurek and Simoneit, 1984](#)). The
232 odd numbered n-alkanes were dominant in the NZ, DR, SH, AZ and JZ samples, with
233 CPI ranging from 1.4 and 2.5, whereas samples from AM, OG, MN and OL showed no
234 significant carbon number preference with CPI of 0.8 to 1.1 ([Table SM1](#)). This odd
235 carbon number preference (CPI >1) of the n-alkanes supported by the C_{max} mainly at 29
236 and/or 31 is distinctive of higher plant waxes (e.g. [Table SM1](#), [Fig. 3b](#), [Buch and](#)
237 [McInerney, 2013](#); [Carr et al., 2014](#)). The contribution of wax n-alkanes were calculated
238 following the method developed by [Simoneit et al. \(1991\)](#) and found to range from 0.01
239 to $0.31 \mu\text{g g}^{-1}$ in these samples.

240 The presence of long chain n-alkanols and minor n-alkanoic acids ($>C_{20}$), with
241 primarily only the even carbon number homologs in the series, is another indicator for
242 plant wax (e.g. [Hitchcock and Nichols, 1971](#); [Simoneit, 1989](#); [Table SM1](#)). The n-
243 alkanolic acids ($<C_{20}$) with a strong even carbon number predominance and C_{max} at 16,
244 are from multiple sources including microbiota and vascular plant waxes, cutin and
245 suberin ([Holloway, 1982](#); [Simoneit, 1989](#)). The absence of unsaturated n-alkanoic acids
246 indicates extensive oxidation and biodegradation of the biomass components in the soils.
247 The even carbon numbered n-alkanols ranging from C_{18} to C_{30} with a C_{max} at 28 and 30
248 are from vascular plant wax typical of desert environments ([Simoneit, 1989](#)). The
249 occurrence of high levels of short chain n-alkanols ($<C_{18}$) with a C_{max} at 10, 11 and 12

250 indicate biodegradation and oxidative processes of the plant wax as well as microbial
251 activities in soils.

252 Steroids can be derived from vascular higher plants, microbial activity in the soil,
253 and cooking in urban areas (Huang and Meinschein, 1976; Rogge et al., 1991). The
254 phytosterols, mainly campesterol, stigmasterol and sitosterol, in the samples from outside
255 the city are derived from vegetation (Simoneit et al., 1983). The presence of cholesterol
256 at relatively high concentrations in most of the soil samples (e.g. AQ, AM, AZ, MN and
257 OL; Table SM1) indicates microbial and/or cooking activities in the area (Rogge et al.,
258 1991; Thompson et al., 2013). The ratio of cholesterol-to-
259 (campesterol+stigmasterol+sitosterol) was used to estimate the dominant sources of
260 sterols in soils (Table SM1). The sites of AQ AM and MN were found to have higher
261 ratios indicating that microbial activities and possibly cooking as a result of evening
262 picnics in these areas were the major sources of sterols.

263 The carbohydrates are comprised mainly of primary saccharides produced by
264 photosynthesis and utilized by biota for energy, with minor metabolites. Complex
265 carbohydrate biopolymers (e.g. cellulose) in soils undergo enzymatic and hydrolytic
266 degradation to simple sugars (i.e., glucose) (Gleixner et al., 2002). Glycerol, the simplest
267 reduced sugar, is derived from the hydrolysis of glyceride lipids and is a significant
268 carbohydrate component of the soils (mean concentration $0.17 \mu\text{g g}^{-1}$, Table SM1). The
269 total saccharide concentrations are low in these soils (0.16 to $3.22 \mu\text{g g}^{-1}$, mean $0.90 \mu\text{g g}^{-1}$;
270 1 , Table SM1), compared to an example from a temperate region (3.77 to $23.71 \mu\text{g g}^{-1}$;
271 Medeiros et al., 2006). Also mycose (a.k.a. trehalose), the recognized fungal saccharide
272 (Niederer et al., 1989), is low compared to sucrose or glucose (Table SM1). This
273 indicates that fungal activity in these soils is minor. The ratio of sucrose-to-mycose was

274 used to explore the microbial/fungal activities in these soil samples. The ratios were low
275 in the sites of DR, OL and MN due greater fungal activity there. Moreover, the small
276 sugar levels in these samples confirm low primary production and alteration of soil
277 biomass.

278 The results of these natural compounds were also analyzed by principal
279 component analysis (PCA) to understand the similarity among these sites in terms of
280 natural components. The PCA analysis output (explaining 98.5% of the variance with an
281 Eigen value of > 1) is shown in Figure 4b where two groups were recognized. The first
282 group included the AQ, AM, NZ, SH, AZ, MN and OL sites (explained by 53.4% as C1
283 dominant) and the second group included the DR, OG and JZ sites (explained by 45.1%
284 as C2 dominant). The former sites are mainly located in areas with less vegetation and
285 relatively high human activities, where the latter sites are located in the city outskirts of
286 Riyadh in areas of relatively low human activities and more vegetation. This indicates
287 that the vegetation cover has an impact on the characteristics and distributions of the
288 natural EOM in the region.

289

290 3.2. Anthropogenic sources

291 Fossil fuel components such as n-alkanes, biomarkers (e.g. hopanes and steranes,
292 Fig. 3c,d and Table SM1), and UCM, as well as the plasticizers (Table SM1 and Fig 3e)
293 indicate anthropogenic inputs from traffic and litter (plastics) (Al-Mutlaq et al., 2002;
294 Rushdi et al., 2005). The n-alkanes with a carbon number predominance of about unity
295 (i.e., CPI ~ 1.0, Bray and Evans, 1961), after subtraction of the wax n-alkane contribution
296 (Simoneit et al., 1991), suggest a source from vehicle/traffic emissions. Crude petroleum,
297 the primary source of gasoline and diesel fuels, and lubricating oils, contains n-alkanes

298 ranging up to about C₃₅ with essentially no carbon number predominance (CPI ~ 1)
299 (Simoneit, 1984) and with lower carbon number maxima in the range of C₂₂ to C₂₅
300 (Simoneit, 1984). These results indicate that fossil fuel utilization is a major input of
301 organic matter to the soil samples, quite obvious for the AM and MN sites (Table SM1).
302 The contribution of total petroleum residues ranges from 0.48 to 98.86 µg g⁻¹ of the total
303 EOM.

304 The presence of hopane and sterane biomarkers in the samples confirms the input
305 from traffic emissions (Simoneit, 1984). Hopanes and steranes are present in exhaust
306 particles from both auto and diesel engines (Simoneit, 1985). This particulate matter falls
307 out and becomes entrained in urban soil. The C-22 S/(R+S) epimer ratios of the
308 homohopanes (C₃₁ and C₃₂), which have been used as maturity indices for petroleum
309 (Seifert and Moldowan, 1978), range between 0.36-0.65 in the soil samples from the city,
310 further indicating the anthropogenic petroleum product inputs (Table SM1). Evidently,
311 crude oil products are one of the major inputs of the OM to the soils. The predominant
312 petroleum component is derived from engine lubricating oil in vehicle emissions, and that
313 with direct oil leakage from vehicles is represented by the UCM (Table SM1). These
314 petroleum residues were detected in samples from areas where truck traffic and industrial
315 factories are major activities (e.g. AM, MN, OG, SH). The absence of levoglucosan and
316 PAHs indicates that organic compounds from biomass burning, i.e., soot fallout
317 (Simoneit et al., 1999) are not a detectable input.

318 Discarded plastics (e.g. shopping bags) are probably the major sources of the
319 plasticizers in the soils of Riyadh, because we have not detected them in blank sample
320 analyses of solvents or the analytical procedures. The contribution of plasticizers in the
321 soil OM ranges from 0.37 to 8.03 µg g⁻¹ of the total EOM.

322 The results of the anthropogenic compounds were also analyzed by the PCA
323 statistical analysis to investigate the similarity among the different sites based on the
324 anthropogenic components. The PCA analysis output (explaining 89.0% of the variance
325 of an Eigen value of > 1) is shown in Figure 4c where two site groups were observed.
326 The first group (C1 and explains 61.9% of variance) included the AQ, NZ, DR, OR, AZ,
327 JZ and OL sites, which are inside the city with relatively more vegetation and
328 landscaping. The second group (C2 and explains 27.1% of the variance) includes only
329 sites AM, SH and MN, which are characterized by the presence of stop stations for large
330 trucks and industrial factories with little vegetation. This indicates that the types of
331 human activities have an impact on the characteristics and the distribution of
332 anthropogenic sources of the EOM in the area.

333 .

334 3.3. Anthropogenic versus natural sources

335 It is obvious that the contribution of natural biogenic versus anthropogenic
336 sources varies and depends on the locations of the soil samples (Fig. 5). The contributions
337 from natural sources (mainly vegetation) ranged from 1.5 to 46.0% of the total EOM in
338 the soils of the city. These values are relatively lower than those reported previously (20-
339 57%, Rushdi et al., 2005). This is attributed to less vegetation and arid conditions in and
340 around Riyadh.

341 The anthropogenic sources were found to range from 54 to 99% of the total EOM.
342 This includes fossil fuel combustion and unintentional crude oil leaks and spills (31 to
343 99%, based on n-alkanes, hopanes, steranes and UCM, and market place and leisure
344 related activities 6% to 39% based on plasticizers, Figs. 5 and 6). The results confirmed

345 that traffic is the major source of detrital anthropogenic OM and pollutants in Riyadh.
 346 Littering is another major source of organic pollutants in soils of the city (Fig. 6).

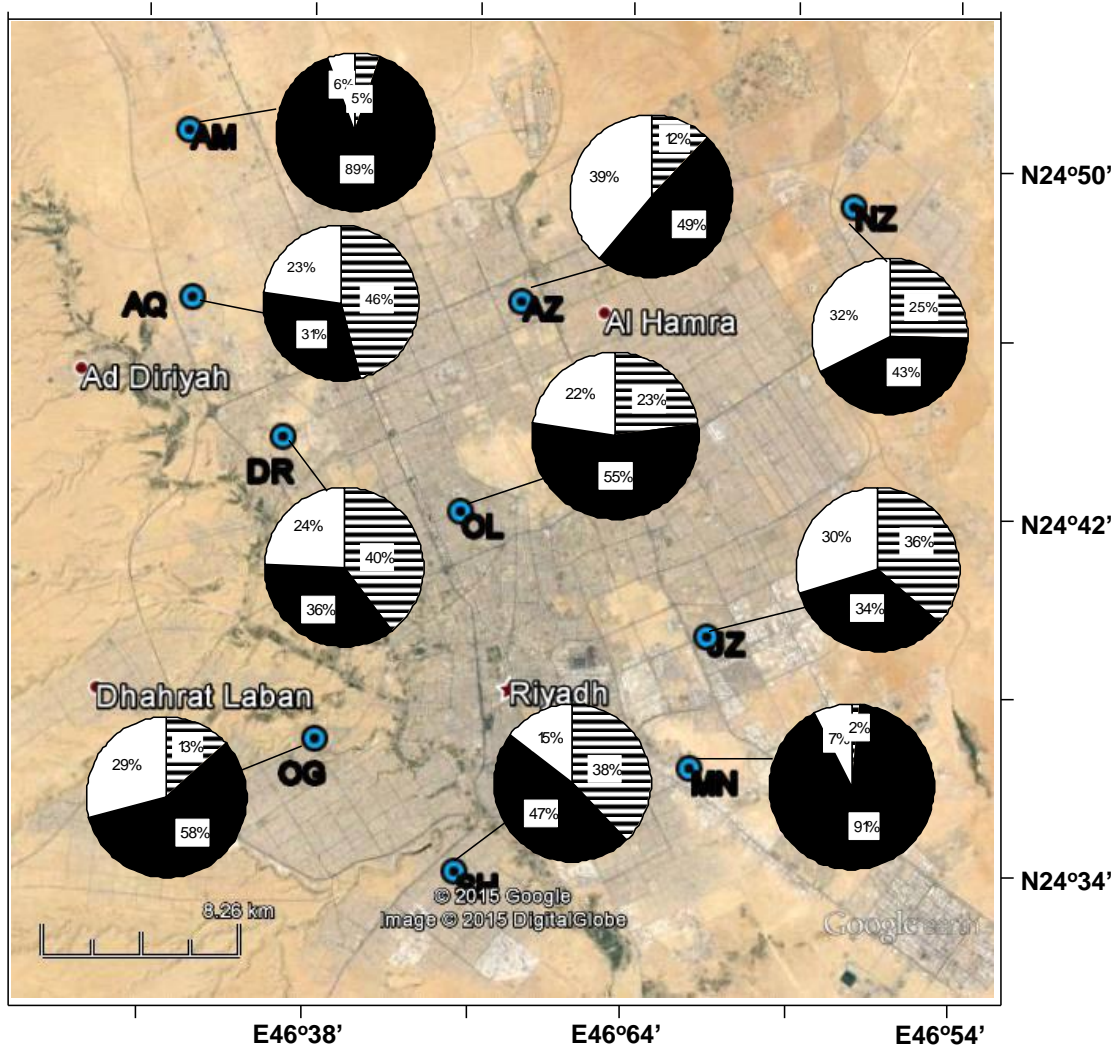


Figure 5. Pi plots of the petroleum residue (black), plasticizers (white) and natural (black and white stripes) fractions at different sites in Riyadh.

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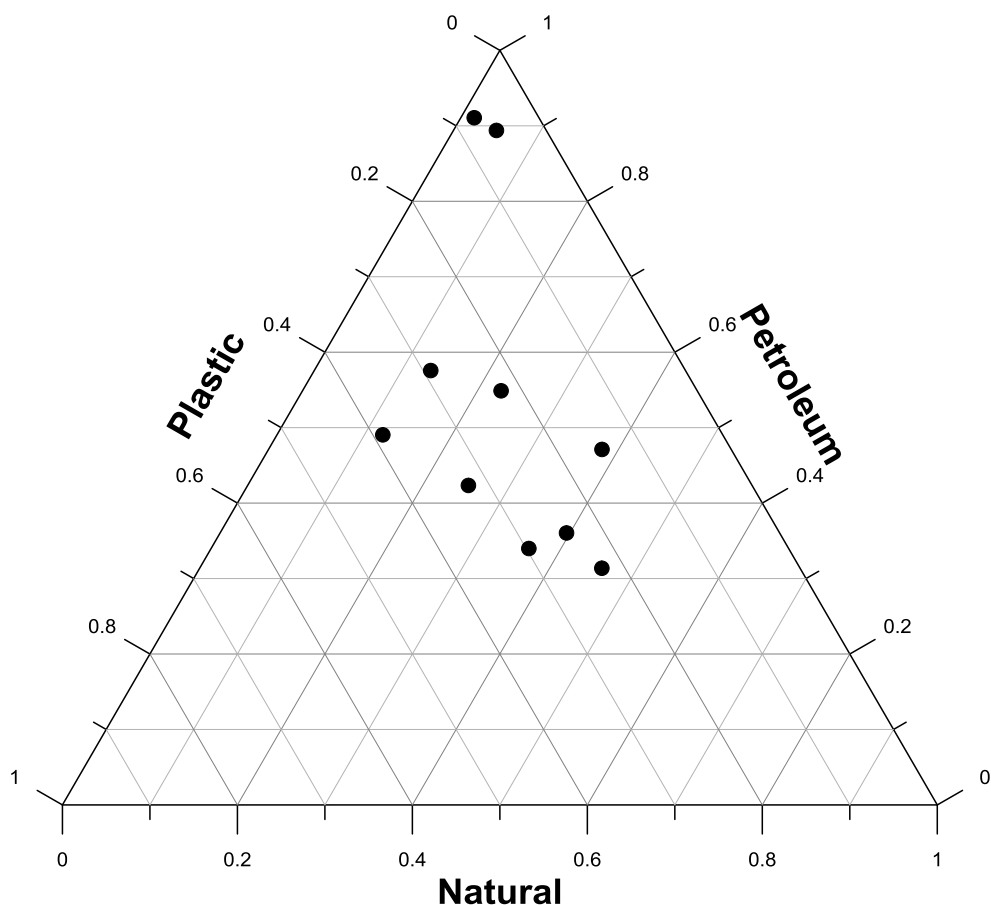


Figure 6. Ternary diagram showing the EOM compound compositions from petroleum residues, plasticizers and natural inputs.

349

350 **4. Conclusions**

351 The analysis of soil samples from the Riyadh metropolitan area showed that both
 352 natural biogenic and anthropogenic sources contributed to their OM contents. The natural
 353 sources of organic compounds are primarily from higher plant wax (i.e., vegetation) and
 354 ranged from 1.5 to 46.0% of the total EOM of the soils. The natural components included
 355 n-alkanols, n-alkanoic acids, n-alkanes (in part), and sterols, with concentrations lower in
 356 the city compared to the surrounding rural areas. **The presence of the natural compounds**

357 from vegetation as major sources refuted the second hypothesis of this research (*the*
358 *sources of natural EOM are relatively low and are primarily from soil microbiota with*
359 *lesser contributions from vegetation.*).

360 The presence of *n*-alkanes with CPI ~1, hopanes, steranes, and UCM from urban
361 traffic emissions and plasticizers from plastic litter and detritus (e.g. shopping bags)
362 characterized the anthropogenic sources, and comprised from 54 to 99% of the total
363 EOM. This, reasonably validated the first hypothesis of this work (*the EOM sources in*
364 *soils of an urban arid region is mainly from traffic emissions*). The abundances of
365 anthropogenic organic compounds in the soils of the city depend on fallout/washout at
366 the sampling location and the types of urban activities.

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372

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