

2018-01

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<http://hdl.handle.net/10026.1/10710>

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10.1016/j.orggeochem.2017.09.004

Organic Geochemistry

Elsevier

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3 **Naphthenic acids in oil sands process waters:**  
4 **Identification by conversion of the acids or esters to**  
5 **hydrocarbons**

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18

19 **Abstract**

20 Concerns over the toxicity associated with ‘naphthenic’ acids (NA) within oil produced  
21 waters and oil sands process waters (OSPW), whether justified or not, have increased the  
22 need for the structural elucidation of NA. Certainly, oil sands mining operations, such as  
23 those in Alberta, Canada, result in the production of large volumes of OSPW contaminated  
24 with NA. Monitoring NA, predicting the toxicities and accounting for the toxicity of residual  
25 NA after clean-up treatments, have all been hindered by the lack of NA identifications.  
26 Recently, a method involving the conversion of the esters of petroleum NA to the  
27 corresponding hydrocarbons before analysis by comprehensive two-dimensional gas  
28 chromatography-mass spectrometry (GC×GC-MS), resulted in the most comprehensive study  
29 of bicyclic NA from petroleum to date. Here, we present results of the analysis by GC×GC-  
30 MS of NA extracted from OSPW after conversion of the acids or ester derivatives to the  
31 corresponding hydrocarbons. The identifications presented include novel alicyclic, aromatic  
32 and sulphur-containing hydrocarbons and thus, by inference, of the corresponding acids. This  
33 supports and significantly extends, previous identifications of OSPW NA as their methyl  
34 esters and can now be used to better inform environmental monitoring programs and toxicity  
35 studies.

36

37 **Keywords**

38 naphthenic acids, GC×GC-TOF-MS, oil sands process water, OSPW

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## 41 **1. Introduction**

42 The identification of individual petroleum or ‘naphthenic’ acids (NA) has proved challenging  
43 for analytical and environmental geochemists for over a century (e.g. Hell and Medinger  
44 (1874)), owing to the complexity and polarity of the isolated acid mixtures. Early research  
45 focused on the role of NA as geochemical markers, their interfacial and corrosive properties  
46 and industrial uses of their metal salts (Seifert, 1975). However, the structural identification  
47 and monitoring of NA has gained considerable interest in recent years, due to concerns over  
48 the presence of NA in oil produced waters and oil sands process waters (OSPW) and their  
49 associated toxicities (Thomas et al., 2009), particularly at the concentrations reported in the  
50 OSPW storage lagoons (e.g. reviewed by Jones et al. (2011); Yue et al. (2015a) and  
51 references therein).

52 Thus, intensive surface mining of bituminous oil sands, such as those of Alberta, Canada,  
53 produces large volumes of OSPW. Despite recycling of the caustic extraction water, large  
54 volumes of process water, contaminated with water-soluble organics from the bitumen, such  
55 as NA, as well as suspended solids, continue to accumulate and are stored in tailings ponds  
56 and lagoons (Kean, 2009).

57 Undiluted OSPW have been shown to be toxic to numerous organisms at the concentrations  
58 found in tailings ponds and since this toxicity has been largely attributed to the NA content  
59 (He et al., 2012; Marentette et al., 2015), considerable effort has been made to develop  
60 methods for monitoring the extremely complex distributions of NA found in OSPW (Frank et  
61 al., 2016). High and ultra-high resolution mass spectrometry methods have revealed that  
62 OSPW contain an extensive range of NA (Yi et al., 2015), beyond so-called ‘naphthenic’ or  
63 cyclic non-aromatic species (Rowland et al., 2014; Barrow et al., 2015). Many analytical  
64 methods also include a chromatographic separation step (e.g. GC or UPLC) (Ortiz et al.,

65 2014; Brunswick et al., 2016; Headley et al., 2016), but most still lack sufficient separation  
66 for identification of individual NA in the OSPW mixtures.

67 However, the use of comprehensive two-dimensional gas chromatography-mass spectrometry  
68 (GC×GC–MS) for the analysis of NA as methyl esters has led to much better separations of  
69 NA mixtures in OSPW. Thus, several bicyclic, tri- and pentacyclic diamondoid acids and  
70 diacids have been identified by comparison of GC×GC retention times and mass spectra with  
71 those of authentic compounds (Rowland et al., 2011b; Rowland et al., 2011d; Lengger et al.,  
72 2013). However, the number of identifications possible was still limited by the complexity of  
73 the acid mixtures, the sparsity of data in current mass spectral databases for relevant esters  
74 and the poor availability of reference compounds for confirmation (Wilde et al., 2015).

75 Recently, a complementary method for the identification of NA was reported in which, after  
76 calibration of the method with model acids, NA were first converted to the corresponding  
77 hydrocarbons (Wilde and Rowland, 2015). This approach, based on refinements of chemical  
78 transformation methods used in early investigations of NA (Seifert et al., 1969), coupled with  
79 analysis of the reduced acids (viz: hydrocarbons) by GC×GC-MS, resulted in the  
80 identification of over 40 individual bicyclic acids in a commercial NA mixture isolated from  
81 petroleum. Identification of the bicyclanes and thus, by inference, of the original bicyclic  
82 acids, was achieved by mass spectral comparison: many more published mass spectra exist  
83 for reference hydrocarbons than for acids or esters (Denisov et al., 1977a; Denisov et al.,  
84 1977b; Denisov et al., 1977c; Golovkina et al., 1984; Petrov, 1987). This made comparisons  
85 of reference mass spectra with those of the unknowns, much more feasible than for the esters.

86 Following the success of the conversion approach on petroleum NA, the current investigation  
87 aimed to apply the same method to the even more complex NA extracts of some OSPW.

## 88 2. Methods

89 Two NA extracts from OSPW tailings ponds from Alberta, Canada, were analysed. Sample  
90 #1 was an NA extract from OSPW collected from the West In-Pit (WIP) tailings pond in  
91 2009, and prepared as described previously (Frank et al., 2006). Briefly, a cleaned-up  
92 concentrated naphthenate solution was obtained by passing the re-dissolved precipitated acids  
93 from OSPW through a diethylaminoethyl-cellulose column (Frank et al., 2006). Sample #2  
94 was OSPW from a second tailings pond. This OSPW was filtered, acidified and extracted in  
95 DCM to provide a crude NA extract (cf. Pereira et al. (2013)).

### 96 2.1. Instrumentation

97 Comprehensive GC×GC-MS analyses were conducted on an Agilent 7890A gas  
98 chromatograph (Agilent Technologies, Wilmington, DE) fitted with a Zoex ZX2 two stage  
99 cooled loop GC×GC modulator and secondary oven (Houston, TX, USA) interfaced with a  
100 BenchTOFdx™ time-of-flight mass spectrometer with an electron impact ionisation source  
101 (Markes International, Llantrisant, Wales, UK). The primary column was a 60 m × 0.25 mm  
102 × 0.25 µm Rxi®-1ms (Restek, Bellefonte, USA), followed by a 1 m × 0.1 mm deactivated  
103 fused silica modulation loop. The secondary column was a 2.5 m × 0.1 mm × 0.1 µm BPX50  
104 (SGE, Melbourne, Australia). Helium was used as carrier gas and the flow was kept constant  
105 at 1.0 mL/min. 1 µL samples were injected at 275 °C splitless. Samples were analysed using  
106 two temperature programmes (referred to as condition sets A and B). Condition set A was  
107 described previously (Wilde and Rowland, 2015) and are given in the Supporting  
108 Information. Condition set B involved the primary oven programmed from 40 °C, held for  
109 1.3 min, then heated to 200 °C at 1 °C/min, to 280 °C at 5 °C/min and to 320 °C at 10 °C/min  
110 and then held for 5 min. The secondary oven was programmed to track the primary oven at  
111 20 °C above. The hot jet was programmed to start 20 °C above the primary oven and finish  
112 100 °C above the primary oven over the period of the run; programmed from 60 °C, held for

113 1 min, then heated to 200 °C at 1.1 °C/min, to 280 °C at 3 °C/min and then to 400 °C at 5  
114 °C/min. Modulation periods of 4 and 6 s were used. The MS transfer line and ion source  
115 temperature were 290 °C and 300 °C, respectively.

116 Data processing was conducted using GC Image™ v2.3 (Zoex, Houston, TX, USA). The  
117 CLIC (Computer Language for Identifying Chemicals) expression tool within GC Image™  
118 v2.3 was used for the determination of the presence or absence of compounds. CLIC  
119 expressions are a powerful tool for applying mass spectral filters and produce advanced  
120 extracted ion chromatograms (EICs) with additional constraints (e.g. Figure 1) (Reichenbach  
121 et al., 2005). Some mass spectral matches were made using NIST Search MS 2.0. Reference  
122 mass spectra obtained from the literature were input into a local NIST library using the NIST  
123 librarian tool to allow mass spectral match quality values to be determined; typically >85 %.

## 124 **2.2. Derivatisation and Fractionation of NA (Scheme 1)**

125 Sample #1 was first derivatised by heating with BF<sub>3</sub>-methanol (BF<sub>3</sub>-MeOH) and the esters  
126 fractionated by argentation (Ag-Ion) chromatography using a method described previously  
127 (Scarlett et al., 2013) and outlined in the Supporting Information. Three fractions were used  
128 for conversion to hydrocarbons; an ‘alicyclic’ fraction (F2) eluting with 100% hexane; an  
129 ‘aromatic’ fraction (F5) eluting with 95 %:5 % hexane:ether and an ‘aromatic/sulphur’-  
130 containing fraction (F7) eluting later with 95 %:5 % hexane:ether. The NA extract of Sample  
131 #2 was not derivatised or fractionated prior to the conversion to the hydrocarbons: i.e. the  
132 free acids were reduced to the hydrocarbons, avoiding the esterification step (Scheme 1).

## 133 **2.3. Conversion of Acids and Esters to Hydrocarbons**

134 Sample #1 (methyl esters) and sample #2 (free acids) were converted to hydrocarbons via the  
135 three-step transformation developed and described previously (Scheme 1) (Wilde and  
136 Rowland, 2015). Briefly, the acids and ester derivatives were reduced using lithium

137 aluminium hydride (LAH) to the primary alcohols. The alcohol products were derivatised to  
138 the p-toluenesulfonate esters using tosyl chloride (TsCl) in the presence of 4-  
139 (dimethylamino)pyridine (DMAP) and triethylamine (TEA). The tosylate products underwent  
140 a ‘SuperHydride®’ reduction with excess lithium triethylborohydride (LiEt<sub>3</sub>BH) to produce  
141 the hydrocarbons. To retain any volatile, low molecular weight products from conversion of  
142 sample #2 (shown by preliminary GC-MS to contain more abundant low molecular weight,  
143 volatile esters), the sample was concentrated to ~1.0 mL using a Kuderna-Danish apparatus,  
144 followed by a simple silica chromatography clean-up step (Wilde and Rowland, 2015). The  
145 masses obtained from the fractionation procedures and the yields of the conversion reactions  
146 are detailed in Tables S1 – S3 in the Supporting Information.

### 147 **3. Results and Discussion**

148 Fractionation of the NA extract of sample #1 by Ag-Ion chromatography (as methyl esters;  
149 Scheme 1), produced ‘alicyclic’ (36 %), ‘aromatic’ (17 %) and ‘aromatic/sulphur’ (4 %) sub-  
150 fractions of OSPW. These contrasted with the proportions of sub-fractions of a commercial  
151 NA extract obtained from the refinement of petroleum (80.0 %, 6.4 % and 0.9 %  
152 respectively) (Wilde and Rowland, 2015) but were consistent with the results of previous  
153 fractionation studies of OSPW NA analysed by liquid chromatography with ion mobility and  
154 high resolution mass spectrometry (Huang et al., 2016).

#### 155 **3.1. Identification of NA after reduction to hydrocarbons**

##### 156 **3.1.1. Adamantane Acids**

157 Previously, tricyclic ‘diamondoid’ or adamantane acids, including diacids, have been  
158 identified in OSPW and oil sands composite tailings pore water, as their methyl ester  
159 derivatives using GC×GC-MS (Rowland et al., 2011b; Bowman et al., 2014; Lengger et al.,  
160 2015). Therefore there is precedent for the identification of adamantane acids within some

161 OSPW NA. Thus, if the conversion of the more complex OSPW NA (free acids or esterified  
162 acids) herein had been successful, analysis of the reduced acid products should lead to the  
163 identification of the corresponding alkyl adamantane hydrocarbons.

164 The mass spectra of alkyl adamantanes are very distinctive and many reference mass spectra  
165 are available in the literature: diamondoid hydrocarbons are commonly used as biomarkers in  
166 petroleum geochemistry (Peters et al., 2005). The spectra of alkyl adamantanes usually  
167 display a dominant or base peak ion corresponding to the loss of the largest alkyl group as a  
168 radical, with the molecular ion for isomers substituted at tertiary carbons displaying a  
169 relatively low intensity molecular ion (approx. 5 – 20 %), compared with isomers substituted  
170 at secondary carbon positions (approx. 30 – 50 %) (Golovkina et al., 1984). The GC elution  
171 order of many dimethyl-, ethyl-, methylethyl- and trimethyl adamantane isomers is  
172 documented (Wingert, 1992; Wei et al., 2006; Wang et al., 2013): typically, alkyl  
173 adamantanes substituted at the secondary carbon positions elute later in GC (and GC×GC)  
174 than isomers substituted at the tertiary positions (Petrov, 1987).

175 The high complexity of the NA extracts from OSPW has hindered previous identifications  
176 and even extracted ion monitoring of the GC×GC data can still result in very complex  
177 chromatograms. However, use of CLIC expressions (cf. Wilde and Rowland (2015)), derived  
178 from the key mass spectral features for alkyl adamantanes, simplified the resulting  
179 chromatograms, displaying more clearly a series of isomers identified as mono- and poly-  
180 substituted alkyl adamantanes by comparison with reference mass spectral data and known  
181 elution orders (Figures 1, S1 and S2).

182 Assignment of the two ethyl isomers of adamantane in the reduced sample #2, after  
183 comparison with the spectra reported by Polyakova et al. (1973) (Ad-II and V; Figure 1; C-F)  
184 also allowed identification of numerous dimethyl- isomers (Figures S1 and S2) based on the

185 comparison of the retention positions, relative to the ethyl isomers. For example, the only two  
186 dimethyladamantane isomers reported to elute between the two ethyl isomers are the cis- and  
187 trans- isomers of 2,4-dimethyladamantane (Wei et al., 2006; Wang et al., 2013). In the  
188 present study this assignment was supported by the high intensity molecular ions (50 – 60 %)   
189 observed in the mass spectra of peaks Ad-III and –IV (Figure S1).

190 The earliest eluting peak (Ad-I) was assigned as 1,2-dimethyladamantane. The absence of  
191 1,3-dimethyladamantane, expected to elute before the 1,2-dimethyl- isomer was consistent  
192 with the absence of 3-methyladamantane-1-carboxylic acid methyl ester, after comparison of  
193 the retention time and mass spectrum of the reference acid methyl ester with the original NA  
194 methyl esters. The adamantane ethanoic acids were also identified in the methyl esters of  
195 sample #2 by comparison of data with those for reference compounds; once more indicating  
196 the complementary nature of the analysis of both the esters and hydrocarbons by GC×GC-  
197 MS. The identification of these acids as the hydrocarbons in the reduced non-methylated,  
198 unfractionated OSPW free NA (#2), also showed that the acids are not artefacts of  
199 esterification.

200 The reduced samples #1 (reduced methyl esters of NA) and #2 (reduced, unesterified free  
201 NA) also showed series of peaks displaying molecular ions at  $m/z$  178, corresponding to C<sub>13</sub>  
202 tricyclic hydrocarbons, many of which had mass spectra matching the reference spectra of  
203 trimethyl- and methylethyl- adamantanes (Figures 1 and S2). The additional clarification of  
204 peaks provided by the CLIC expression chromatogram, allowed comparison of the retention  
205 positions of the C<sub>13</sub> adamantane isomers with those reported in the literature to aid  
206 identification (Figure 1; A and B).

207 These results confirmed that the conversion of OSPW NA mixtures to the corresponding  
208 hydrocarbons was successful, despite the increased complexity compared to the petroleum

209 acid mixtures analysed previously (Wilde and Rowland, 2015). Thus, due to the widely  
210 available reference spectra and the known elution orders of numerous alkyl adamantanes,  
211 conversion of the OSPW NA as acids or esters, to the corresponding hydrocarbons,  
212 confirmed the presence of known acids, the presence of acids that were only tentatively  
213 assigned previously and also resulted in the identification of numerous new acids.

### 214 **3.1.2. Bicyclic Acids**

215 Alicyclic bicyclic acids are a major class of OSPW NA. High- and ultra-high resolution mass  
216 spectrometric techniques often show ions corresponding to  $C_nH_{2n-4}O_2$  acid species with  
217 carbon numbers (n) ranging from  $C_{9-20}$ , as the most abundant  $C_nH_{2n+z}O_2$  species (z, hydrogen  
218 deficiency due to cyclicity) (Barrow et al., 2010). Analysis of commercial and OSPW NA  
219 methyl esters by GC×GC-MS has shown that the ions detected by high resolution mass  
220 spectrometry alone represent hundreds of different structural isomers (Damasceno et al.,  
221 2014; Wilde et al., 2015). Based on the limited knowledge of bicyclic acids, a well-accepted  
222 screening assay reported some bicyclic acids to be the most toxic of those studied (Jones et  
223 al., 2011; Yue et al., 2015b). Scott et al. (2008) showed the ozonation of OSPW resulted in  
224 the removal of most bicyclic acids ( $C_nH_{2n-4}O_2$  species); however, little is known about the  
225 residual acids, or of any transformation products.

226 Investigations into the structural identification of bicyclic acids resulted in the first  
227 identification of novel bridged bicyclic acids, along with several bicyclic fused and  
228 terpenoid-derived acids (Wilde and Rowland, 2015; Wilde et al., 2015). In the current  
229 investigation, analysis of the ‘alicyclic’ acids as methyl esters of sample #1 and the  
230 unfractionated acid methyl esters of sample #2, revealed homologous series of isomers with  
231 mass spectra displaying molecular ions consistent with that of  $C_{11-16}$  and  $C_{10-15}$  bicyclic acids  
232 respectively, as reported as typical of OSPW NA (Hindle et al., 2013). Careful concentration  
233 of the hydrocarbon product of sample #2, following reduction of the unfractionated NA,

234 using a Kuderna-Danish apparatus and subsequent analysis by GC×GC-MS showed  
235 homologous series of C<sub>10-15</sub> bicyclanes (Figure S3; A and B).

236 Despite the complexity of sample #2, comparison of the mass spectra of those bicyclanes  
237 which were not hindered by co-elution effects, resulted in the identification of  
238 bicyclo[3.2.1]octane, bicyclo[3.3.0]octane and bicyclo[4.3.0]nonane alkyl derivatives (Figure  
239 2 and S3). For example, the earliest eluting isomer (**bi-I**) was assigned as 1,4-  
240 dimethylbicyclo[3.2.1]octane (Figure 2; A and B) after comparison with reference mass  
241 spectra (Denisov et al., 1977a). The same bicyclane, and by inference the same acid, was  
242 identified previously in petroleum-derived NA (Wilde and Rowland, 2015).

243 Comparison of the mass spectrum of isomer bi-II with the mass spectra of alkyl  
244 bicyclo[3.3.0]octanes resulted in the identification of 1,2-dimethylbicyclo[3.3.0]octane  
245 (Figure 2; C and D) (Denisov et al., 1977c). This assignment was supported by its retention  
246 position relative to 1,4-dimethylbicyclo[3.2.1]octane (bi-I) which matched the elution order  
247 of C<sub>10</sub> bicyclanes reported previously (Piccolo et al., 2010) and complemented the  
248 identification of several bicyclo[3.3.0]octane acids in petroleum-derived NA (Wilde and  
249 Rowland, 2015). However, this was the first identification of a bicyclo[3.3.0]octane acid in  
250 NA with a substituent at a bridgehead carbon.

251 The isomer bi-III displayed a mass spectrum matching those of *cis-cis* and *trans-cis* 3-  
252 methylbicyclo[4.3.0]nonane (Figure 2; E and F) (Denisov et al., 1977b). Numerous  
253 methylbicyclo[4.3.0]nonanes were identified in the petroleum NA (Wilde and Rowland,  
254 2015) with the isomer assigned as the *cis-cis/trans-cis* 3-methyl- isomer eluting earliest of all  
255 the 2- and 3-methyl- isomers. The mass spectra of the later eluting isomers bi-IV to VI were  
256 difficult to assign. The isomer bi-IV was tentatively assigned as 2,6-  
257 dimethylbicyclo[3.2.1]octane (Figure S3; C and D) and the mass spectra of the remaining

258 bicyclanes, e.g. bi-V and VI (Figure S3; E and F), did not match any of the reference spectra,  
259 which encompassed an extensive range of bicyclane isomers.

260 Petroleum NA and NA extracted from OSPW have often been reported to possess  
261 significantly different compositions (Grewer et al., 2010). This is often observed as  
262 differences in the HPLC retention times of the unresolved NA ‘humps’ (OSPW NA eluting  
263 slightly earlier) (Han et al., 2008). The differences are also reflected in the increased  
264 resistance of OSPW NA to biodegradation; suggested to be because the OSPW NA possess  
265 more highly branched carboxylated side chains (Misiti et al., 2014; Brown and Ulrich, 2015).  
266 However, this speculation has never been supported by the identification of the acids. The  
267 presence of aromatics in OSPW NA, may have an important role in the differences in  
268 retention time and toxicity observed for different NA mixtures (Jones et al., 2012), but  
269 aromaticity obviously does not explain the observations made for these alicyclic acids.

270 A complementary explanation suggested here is that the OSPW NA examined herein instead  
271 possess a higher proportion of condensed, bridged structures, substituted at different positions  
272 e.g. bridgehead carbon (Figure 2; A-D). Differences between the bicyclic acids, identified as  
273 the corresponding bicyclanes, in petroleum NA and OSPW NA included the position of  
274 substituents (e.g. bridgehead substituted isomers present in OSPW, Figure 2; C), as well as  
275 the presence of some unknown bicyclic acid isomers detected in OSPW, but not detected in  
276 petroleum NA (e.g. Figure S3). The suggestion is supported by the fact that bridged  
277 compounds elute earlier than fused ring acids (e.g. decalin acids) and is reinforced by the  
278 identification of bicyclo[2.2.1]heptane acids in OSPW and the reported elution order of  
279 reference acids (Wilde et al., 2015). Bicyclo[2.2.1]heptane acids are the earliest eluting of  
280 any the bicyclic acids previously analysed, which were not detected in petroleum NA as the  
281 methyl esters, or corresponding bicyclanes (Wilde and Rowland, 2015; Wilde et al., 2015).

282 These structural differences may also help explain the differences in toxicity of some NA  
283 mixtures.

284 Despite recent advances in spectrometric studies on OSPW and NA (Headley et al., 2016),  
285 few examples exist which have provided structural evidence for the observed compositional  
286 differences between different NA mixtures based on the identification of individual acids  
287 (Swigert et al., 2015). Following the identifications herein; representative NA can now be  
288 used to quantify the relative proportions of bicyclic species by high resolution methods;  
289 relevant acids can be synthesised and the toxicities measured (Yue et al., 2015b).

### 290 **3.1.3. Non-Diamondoid Tricyclic Acids**

291 Apart from the adamantane acids, few tricyclic acids have been identified in OSPW to date.  
292 The mass spectra of isomers tt-I to -VI all displayed fragmentation patterns characteristic of  
293 those of tricyclic terpane hydrocarbons (Figure S4). Ekweozor and Strausz (1982) reported  
294 the identification of a series of C<sub>19-30</sub> tricyclic terpanes present in bitumen from the Athabasca  
295 oil sands with a cheilanthane ‘core’, with the branched alkyl side chain substituted at position  
296 14 (Figure S4; F). Based on the molecular ions, in the mass spectra of the hydrocarbons tt-I to  
297 -VI, the series included two C<sub>20</sub> (tt-I and -II), two C<sub>21</sub> (-III and -IV), one C<sub>23</sub> (-V) and one C<sub>24</sub>  
298 (-VI) compound (Figure S4). The structures were proposed to possess cheilanthane ‘cores’,  
299 methyl- substituted in the 13-position with a branched alkyl chain substituted in the 14-  
300 position. However, the exact position of the alkyl chain, or carboxylated side chain in the  
301 original acids, is a subject of debate (Cyr and Strausz, 1983).

### 302 **3.1.4. Tetracyclic and Pentacyclic Acids**

303 The presence of tricyclic diamondoid acids in OSPW was proposed to be, at least partly, due  
304 to the biotransformation of the corresponding hydrocarbons (Rowland et al., 2011b).  
305 Pentacyclic diamondoid hydrocarbons, such as diamantane and alkyl diamantanes have also

306 been reported in various crude oils and were reported to be much more resistant to  
307 biodegradation compared to the adamantane homologues (Wang et al., 2006).

308 However, some pentacyclic diamondoid acids have also been detected in OSPW (Rowland et  
309 al., 2011d). The occurrence of these acids was suggested to occur from the biodegradation of  
310 the corresponding alkyl diamantanes and that their presence was evidence for biodegradation  
311 (Rowland et al., 2011d). Following the successful conversion and identification of the alkyl  
312 adamantanes herein (and thus alkyl adamantane acids), the hydrocarbons of both reduced  
313 samples #1 (reduced esters of NA) and #2 (reduced free acid NA) were examined for isomers  
314 of penta- and tetracyclic ‘diamondoids’.

315 Reference spectra for diamantane hydrocarbons, whilst fewer than those of the adamantanes,  
316 are as distinctive, due the stability of the cage-like core, (e.g. displaying base peak ions due to  
317 the loss of an alkyl radical and intense molecular ions for isomers with the alkyl substituent  
318 on a secondary carbon position). Comparison of the reference mass spectra of 1-, 3- and 4-  
319 methyladamantanes and their GC elution order (Wingert, 1992; Wang et al., 2013), allowed  
320 the identification of all three isomers in sample #2 and of 3-methyladamantane in sample #1  
321 (Figure S5; B).

322 Extracted ion monitoring of the key fragment ions revealed a series of isomers assigned as  
323 alkyl diamantanes (diA-I to diA-XXV) ranging from C<sub>15-18</sub> based on the observed molecular  
324 ions (Figure S5). Interpretation of the mass spectra of peaks diA-I to -XXV (examples are  
325 shown in Figure S5; B-H), resulted in the assignment of isomers of ethyl- (D), dimethyl- (E),  
326 ethylmethyl- (F and G) and dimethylethyl- (H) diamantanes. These results provided strong  
327 supporting evidence for the array of highly substituted alkyl diamantane acids previously  
328 speculated to be present in OSPW (Rowland et al., 2011d).

329 Tetracyclic acids were also tentatively assigned previously based on mass spectral  
330 interpretation of the spectra of the methyl esters (Rowland et al., 2011d). The tetracyclic  
331 acids were proposed to possess ring-opened diamantane structures (Figure S6; A). However,  
332 comparison of the retention positions and mass spectra of synthetic reference acids with those  
333 of NA within OSPW, did not confirm their identification (Rowland et al., 2011a).

334 Series of peaks were observed in the hydrocarbon products obtained from both samples #1  
335 and #2 herein, with spectra with molecular and base peak ions consistent with C<sub>14-18</sub>  
336 tetracyclic hydrocarbons, and some additional C<sub>13</sub> isomers in the reduced sample #2 (Figures  
337 S7 and S8). The mass spectra were very similar to those of alkyl adamantanes and alkyl  
338 diamantanes, dominated by a base peak ion presumably corresponding to the loss of the  
339 largest alkyl substituent and suggesting a highly stable core (Figures S7 and S8). These  
340 hydrocarbons were presumed to originate from tetracyclic acids, such as those previously  
341 tentatively assigned (Rowland et al., 2011d). Subsequent examination of data for the original  
342 acid methyl esters indeed showed isomers across the same carbon number range, with mass  
343 spectra similar to those previously reported in other OSPW samples (Figure S9) (Rowland et  
344 al., 2011d).

345 The lowest carbon number isomers (C<sub>13-14</sub>) displayed base peak ions at *m/z* 161 (Figure S7;  
346 B-D). Assuming the compounds possess ‘adamantanoid-like’ structures, this indicated a C<sub>12</sub>  
347 ‘core’; *m/z* 161 (100 %) corresponding with a C<sub>12</sub>H<sub>17</sub><sup>+</sup> highly stable cation. The only alkyl  
348 (tetracyclic) ‘adamantanoid’ structures with a C<sub>12</sub> core, previously assigned in crude oils, are  
349 alkyl 2,4-cyclopentano-adamantanes (Petrov, 1987). Other stable, non-adamantanoid  
350 tetracyclic structures, such as bridged or highly condensed cyclopentyl structures would not  
351 allow for isomers with carbon numbers as low as C<sub>13</sub> and the few reference mass spectra  
352 available were significantly different (Vorob'eva et al., 1986).

353 Analysis of the reduced acid, hydrocarbon products herein therefore provides the first  
354 evidence for a firmer assignment of the tetracyclic acids as possessing cyclopentano-  
355 adamantane cores e.g. 2,4-cyclopentano-adamantane acids (Figure S6; B and C), at least for  
356 some of the higher carbon number homologues. Subsequent re-examination of the  
357 unfractionated OSPW NA as their acid methyl esters, did indeed reveal esters with mass  
358 spectra consistent with those of the corresponding cyclopentano-adamantane acids (Figure  
359 S9).

### 360 **3.1.5. Monoaromatic Acids**

361 Fraction 5 from the argentation fractionation of sample #1, was selected for conversion to the  
362 hydrocarbons since it was rich in aromatic acids, as indicated by infrared spectroscopy  
363 (FTIR), strong UV absorption and adsorption to silver ions in argentation chromatography  
364 (Jones et al., 2012). The ‘aromatic’ acids have been shown to have similar acute toxicity to  
365 the ‘alicyclic’ acids but only produce a weak estrogenic effect in zebrafish larvae (Scarlett et  
366 al., 2013).

367 Rarely cited early investigations of petroleum NA, also showed that aromatic acids were  
368 present (Knotnerus, 1957), but the use of the term ‘naphthenic’ to describe the acids appears  
369 to have led most recent workers to overlook the relevance of the aromatic species. Even with  
370 this realisation (Rowland et al., 2011c; Jones et al., 2012; Bowman et al., 2014), very few  
371 aromatic acids have been firmly identified in OSPW to date.

372 However, using the mass spectral characteristics of aromatic hydrocarbons to aid assignments  
373 herein, series of peaks were assigned as monoaromatic species (Figure S10). The base peak  
374 ions in the mass spectra of isomer ma-I to -IV (e.g.  $m/z$  105, 119, 133) suggested these  
375 consisted mainly of di-, tri- and tetramethylalkylbenzenes (McLafferty, 1963). The presence  
376 of many fragment ions (e.g.  $m/z$  175, 161 and 147) suggested they did not possess straight n-

377 alkyl chain substituents, since the spectra were dissimilar from those reported (Ji-Zhou et al.,  
378 1993). The lack of intense ions at  $m/z$  106, 120 and 134 (from  $\gamma$ -hydrogen transfer as opposed  
379 to benzylic or  $\beta$ -cleavage) also implied that either, the alkyl chain was not methyl-substituted  
380 at the  $\gamma$ -position or, that both ortho- positions on the benzene ring were substituted  
381 (Sinninghe Damsté et al., 1988). Some of the mass spectra closely resembled those reported  
382 for monoaromatic hydrocarbons identified as alkylbenzenes obtained from artificially  
383 matured melanoidins (Larter et al., 1981). This evidence implied that the corresponding  
384 alkylbenzene alkanolic acids were OSPW NA.

385 Since alkylbenzenes are common pollutants and conceivably might also be hydrocarbon  
386 contaminants in the OSPW, the corresponding acid methyl esters were searched for in the  
387 esterified OSPW NA, based on the expected retention differences observed between the acid  
388 methyl esters and the hydrocarbons (Figure S11). The acids (methyl esters) were indeed  
389 present. The similarity in mass spectra between the alkylbenzene hydrocarbons and acids  
390 (e.g. Figure S12) indicated that the carboxylate moiety was at the end of an alkyl side chain  
391 and not directly substituted onto the benzene ring, consistent with the current understanding  
392 of bacterial degradation of branched alkyl hydrocarbons (Misiti et al., 2014).

393 Recently, the methyl esters of C<sub>11</sub> indane-2-acetic acid and tetralin-2-carboxylic acids were  
394 identified, following derivatization, in oil sands composite tailings pore water (Bowman et  
395 al., 2014). Such low molecular weight acids were not present in the OSPW aromatic fraction  
396 of sample #1 under study herein and hence were not observed in the hydrocarbon reduction  
397 products. Nonetheless, series of larger C<sub>14-20</sub> branched alkyl indanes and tetralins were  
398 tentatively identified (mb-I-VI) by comparison of the spectra in the NIST mass spectral  
399 library and with available literature mass spectra (Figure S13) (Booth et al., 2006 ). These  
400 identifications imply that the corresponding indane and tetralin alkanolic acids, not known  
401 previously, were present in OSPW.

402 Numerous tricyclic monoaromatic acids were present in OSPW NA, though the only acid to  
403 be assigned to date is dehydroabiatic acid (DHAA) (Jones et al., 2012). One compound (tm-I)  
404 with a mass spectrum which was similar to that of the corresponding hydrocarbon,  
405 dehydroabietane, was identified in the OSPW hydrocarbons obtained from reduction of the  
406 ‘aromatic’ fraction of sample #1 (Figure S14; A and B). However, the spectrum of tm-I was  
407 even more similar to that of the C<sub>19</sub> and isomeric C<sub>20</sub> hydrocarbons 13,14-dimethyl- and 13-  
408 methyl-14-ethylpodocarpa-8,11,13-triene (Figure S14; C and D) (Azevedo et al., 1990). This  
409 was supported by a subsequent retro-examination of the aromatic acid methyl esters of this  
410 fraction, which failed to reveal the presence of DHAA methyl ester in this OSPW sample (*cf.*  
411 unlike a different OSPW sample examined by Jones et al. (2012)).

412 Identification of the corresponding alkyl substituted podocarpa-8,11,13-triene acid has not  
413 been previously reported in OSPW NA. However, Azevedo et al. (1994) reported the  
414 presence of a series of C<sub>19-30</sub> tricyclic C-ring monoaromatic carboxylic acids possessing the  
415 same structure, with the alkanooate chain in the 14-position in Tasmanian tasmanite (marine  
416 type shale).

### 417 **3.1.6. Diaromatic Sulphur-Containing Acids**

418 Fraction 7 from the fractionation of sample #1, was selected because it is a sulphur-rich,  
419 aromatic fraction of OSPW NA for conversion to hydrocarbons (West et al., 2014). The latter  
420 authors West et al. (2014) tentatively assigned five C<sub>16-18</sub> diaromatic sulphur-containing acids  
421 as possessing methyl substituted dibenzothiophene or dimethylnaphthothiophenes (or  
422 dimethyldibenzothiopyrans) with methyl branched propanoate acid side chains. Despite  
423 comparison of the GC×GC retention times and mass spectra with those of reference  
424 dibenzothiophene acid methyl esters and rigorous mass spectral interpretation, none were  
425 firmly identified in that study.

426 Examination of the 'aromatic/sulphur'-containing fraction of acid methyl esters analysed  
427 herein by GC×GC-MS indeed revealed the five C<sub>16-18</sub> isomers reported by West et al. (2014).  
428 Following reduction, the corresponding sulphur-containing hydrocarbons were detected,  
429 possessing mass spectra similar to those of the original acid methyl esters (e.g. dominated by  
430 base peak ions at *m/z* 197, 211 and 225), corresponding to the loss of ·C<sub>3</sub>H<sub>7</sub> (Figure 3 and  
431 S15). Application of a CLIC expression (Figure 3; B) enabled clear mass spectra to be  
432 obtained for interpretation and comparison with reference spectra and compounds. The only  
433 structure possible for the alkanoate side chain of these isomers, consistent with the loss of M-  
434 87 and the absence of a radical cation produced from a McLafferty rearrangement in the mass  
435 spectra of the methyl esters (West et al., 2014), along with the consistent loss of ·C<sub>3</sub>H<sub>7</sub> by  
436 benzylic cleavage in the mass spectra of the hydrocarbons, was that of a dibenzothiophene (or  
437 naphthothiophene) containing an isobutyl side chain. The retention position and mass  
438 spectrum of synthesised 4-isobutyldibenzothiophene matched that of the dbt-I isomer,  
439 confirming its identification (Figure 3; C and D), and by inference, the identification of  
440 dibenzothiophene-4-isobutanoic acid in OSPW NA.

441 West et al. (2014) also reported the presence of sulphur-containing acids with 8 and 9 double  
442 bond equivalents (DBE), eluting slightly earlier than those compounds possessing 10 DBE  
443 now identified as dibenzothiophene acids. Examination of the F7 hydrocarbon product  
444 herein, revealed a series of isomers with spectra displaying molecular ions consistent with  
445 diaromatic sulphur-containing hydrocarbons with 8 DBE (e.g. *m/z* 214, 228, 242 and 256),  
446 eluting slightly earlier than the 10 DBE dibenzothiophenes (e.g. isomer nat-1 in Figure 3; A).  
447 The mass spectra of these isomers (nat-1 to -V) were dominated by intense base peak ions at  
448 *m/z* 171 and 185, with very few fragment ions observed (Figure S16). This indicated that the  
449 compounds were highly condensed, with the base peak ion most likely formed via benzylic  
450 cleavage of an alkyl substituent. Comparison of the mass spectrum of the isomer nat-I, with

451 reference spectra in the NIST MS Library, showed that the spectrum was similar to that of 2-  
452 methyl-2H-naphtho[1,8-bc]thiophene (Figure S16; A and B). The NIST mass spectrum  
453 showed a loss of M-15, attributed to fragmentation of the methyl substituent, via benzylic  
454 cleavage, as proposed previously for the fragmentation of alkyl 2H-naphtho[1,8-  
455 bc]thiophenes (Figure S16; A) (Porter, 1985).

456 The mass spectrum of nat-I displayed a similar fragmentation pattern and ions to that of the  
457 NIST reference spectrum. However, with the base peak ion of nat-I corresponding to the loss  
458 of M-43 instead, this was attributed to the loss of a propyl group  $\cdot\text{C}_3\text{H}_7$  (Figure S16; B). The  
459 mass spectra of naphtho[1,8-bc]thiophene acids would be expected to display similar mass  
460 spectral fragmentation patterns (due to the stability of the condensed structure) with  
461 additional radical cations due to McLafferty rearrangement of the alkanoate side chain,  
462 involving the hydrogen on the carbon adjacent to the sulphur atom. Subsequent re-  
463 examination of the OSPW F7 NA methyl esters indeed revealed a series of peaks with mass  
464 spectra displaying fragmentation patterns similar to those of the nat-I to -V hydrocarbons,  
465 with additional even mass ions, corresponding to M-74, M-88 and M-102 ions (Figure S17),  
466 attributed to neutral losses from hydrogen rearrangement on the alkanoate side chain. These  
467 observations, coupled with the spectral interpretation; similarity with the reference spectrum  
468 (Figure S16; A and B); retention position relative to the dibenzothiophenes and precedent for  
469 the presence of sulphur-containing acids with 9 DBE confirmed by GC $\times$ GC with sulphur  
470 chemiluminescence detection and high resolution mass spectrometry (West et al., 2014), led  
471 to the tentative assignment of naphtho[1,8-bc]thiophene acids in OSPW NA herein.

472 Sulphur-containing hydrocarbons possess the same nominal mass as some aromatic  
473 hydrocarbons and could be misassigned when analysed by unit resolution mass spectrometric  
474 techniques (Hegazi and Andersson, 2007). However, interpretation and comparison of the

475 mass spectra of such hydrocarbons, clearly ruled them out as possibilities for those discussed  
476 above.

#### 477 **4. Conclusions**

478 The identifications presented herein of individual hydrocarbons and thus acids in OSPW,  
479 included alicyclic, aromatic and sulphur-containing NA. The assignments were consistent  
480 with, but expanded upon, previous evidence of such acids in other matrices, identified as the  
481 esters (Rowland et al., 2011b; Rowland et al., 2011d; West et al., 2014; Wilde et al., 2015)  
482 and were supported by the identification of multiple isomers of each acid type. The acids  
483 identified can perhaps be used to better inform environmental monitoring programs as well as  
484 for geochemical and toxicity studies. The same approach may have wide applicability to  
485 other polluted waters and functionalised organic compounds in sediments and petroleum.

#### 486 **Supplementary Material**

487 Mass spectra of all identified hydrocarbons and a summary of all identifications made are  
488 provided in the Supplementary Material (Table S4 and Figures S1-S17).

#### 489 **Acknowledgements**

490 Funding of this research was provided by an Advanced Investigators Grant (no. 228149)  
491 awarded to SJR for project OUTREACH, by the European Research Council, to whom we  
492 are extremely grateful. We would also like to thank Plymouth University for a funding  
493 contribution to MJW. We thank Dr C. Anthony Lewis for invaluable discussions and Dr  
494 Charles E. West, Dr Alan G. Scarlett and Will Robson (all then Plymouth University, UK)  
495 for helping with GC×GC-MS operation. Finally we thank Dr Laurent C. Piccolo (Université  
496 Claude Bernard Lyon 1, France) for providing some hydrocarbon mass spectra and we thank  
497 Drs L. M. Hewitt and R. Frank (Environment Canada) and Professor J. Martin (University of  
498 Alberta, Canada) for the samples of OSPW extracts.

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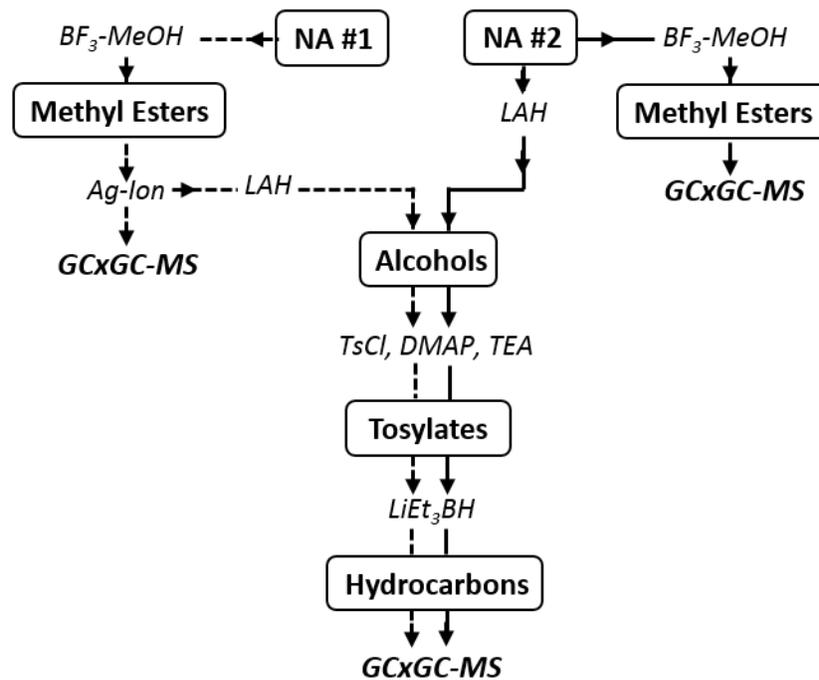
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Scheme 1: Route of conversion of the OSPW NA samples #1 and #2, to the corresponding hydrocarbons.



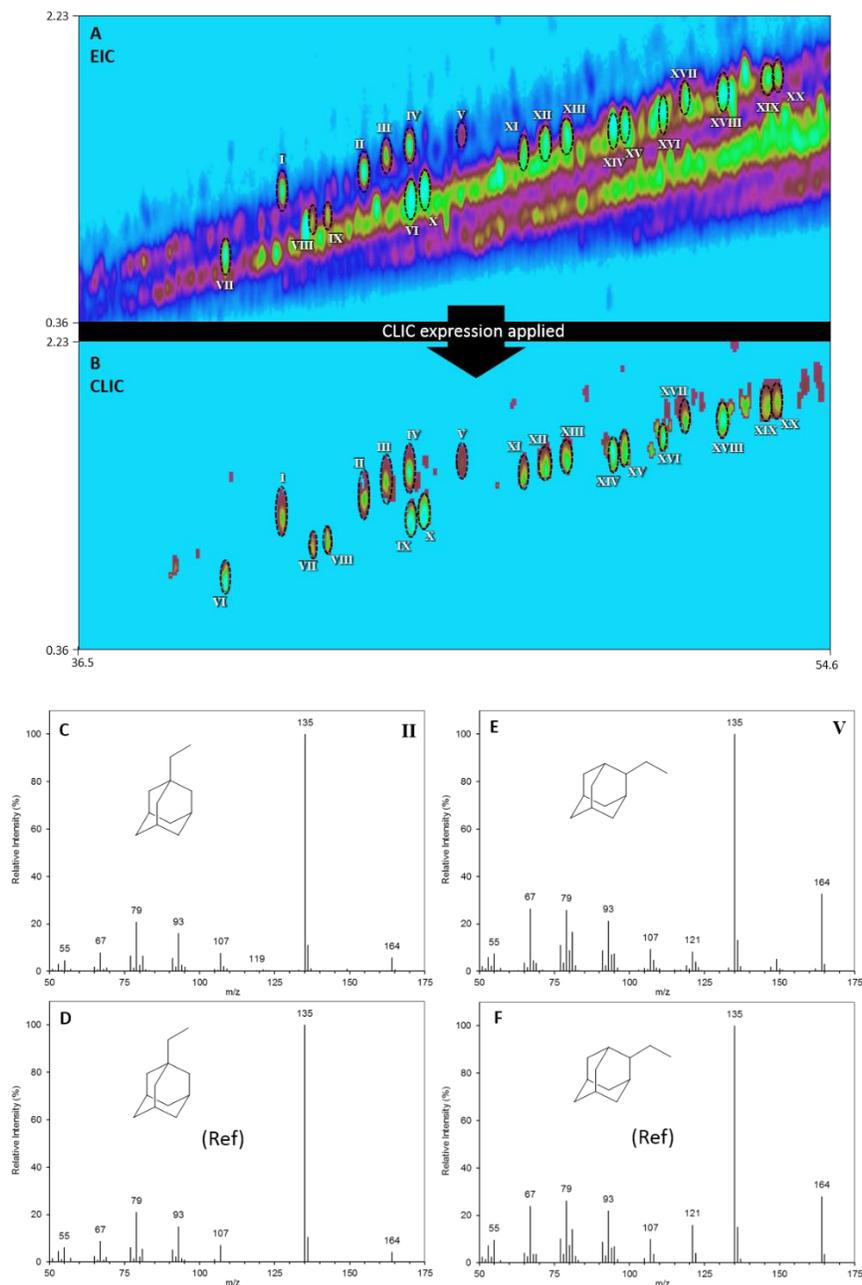


Figure 1: Comparison of (A) an EIC ( $m/z$  135, 149, 163 and 178) and (B) a simplified chromatogram after a CLIC expression was applied of the reduced unfractionated OSPW sample (#2), clearly showing the presence of three dimethyl- (Ad-I, -III and -IV), (C-F) two ethyl- (-II and -V), eight trimethyl- (-VI-VIII, -X-XIII and -XVII) and seven ethylmethyl-adamantane isomers (-IX, -XIV-XVI and -XVIII-XX), based on comparison with reference mass spectra and known elution order (Polyakova et al., 1973; Wingert, 1992; Wang et al., 2013).

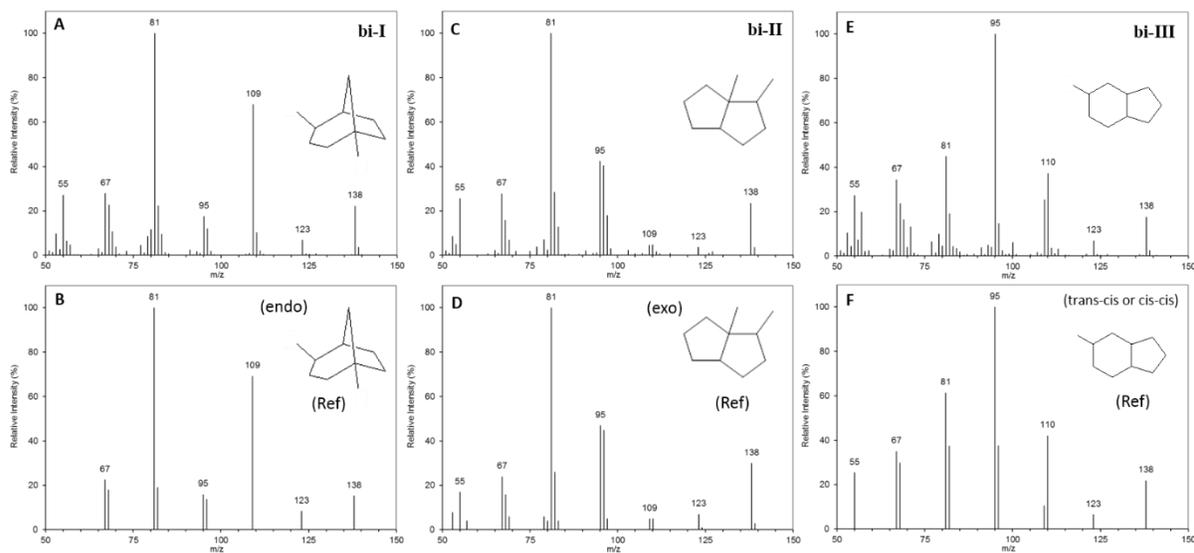


Figure 2: Identification of bridged and fused bicyclanes by mass spectral comparison with reference spectra and elution order (Denisov et al., 1977a; Denisov et al., 1977b; Denisov et al., 1977c).

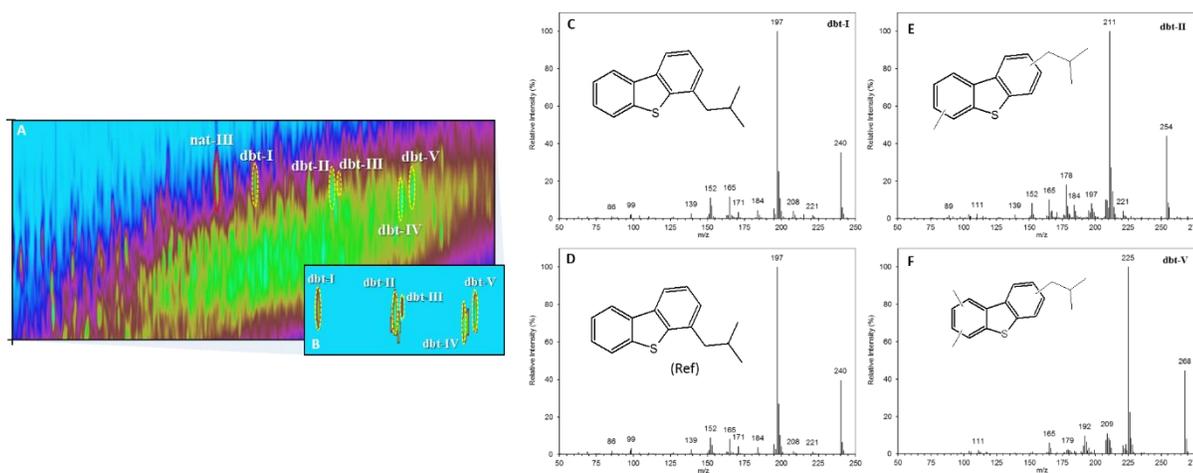


Figure 3: (A-B) TIC and CLIC EIC of reduced 'aromatic/sulphur' fraction (sample #1), showing isomers dbt-I to -V assigned as the reduced hydrocarbons of the five methyl esters reported by West et al. (2014). (C) Identification of dbt-I after comparison with (D) synthesised 4-isobutyldibenzothiophene and (E-F) assignment of dbt-II and -V as methyl- and dimethyl- isobutyldibenothiophenes.

## SUPPORTING INFORMATION FOR PUBLICATION

### Naphthenic acids in oil sands process waters: Identification by conversion of the acids or esters to hydrocarbons

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## REFERENCES (P. S-23)

## SUPPORTING INFORMATION EXPERIMENTAL DETAILS

### 4.1. GCxGC-MS

The GCxGC-MS conditions set A involved the primary oven programmed from 30 °C, held for 1 min, then heated to 120 °C at 5 °C/min, to 220 °C at 0.8°C/min, to 280 °C at 5 °C/min and to 320 °C at 10 °C/min and then held for 10 min. The secondary oven was programmed to track the primary oven at 40 °C above. The hot jet was programmed to start 30 °C above the primary oven temperature until 150 °C, it was then ramped to 260 °C at 1.3 °C/min and then to 400 °C at 4 °C/min. The modulation period was set 4 and 6 s. The GCxGC-MS conditions set B involved the primary oven programmed from 40 °C, held for 1.3 min, then heated to 200 °C at 1 °C/min, to 280 °C and 5 °C/min and to 320 °C at 10 °C/min and then held for 5 min. The secondary oven was programmed to track the primary oven at 20 °C above. The hot jet was programmed to start 20 °C above the primary oven and finish 100 °C above the primary oven over the period of the run; programmed from 60 °C, held for 1 min, then heated to 200 °C at 1.1 °C/min, to 280 °C at 3 °C/min and then to 400 °C at 5 °C/min. The modulation period was set at 4 and 6 s.

### 4.2. Derivatisation and fractionation of sample #1

A concentrated naphthenate solution, extracted from oil sands process-affected water (OSPW), which had undergone a prior clean-up procedure involving weak anion exchange chromatography, was received from Environment Canada, Burlington, CA. The extraction and clean-up procedure was developed and reported by Frank et al. (2006).

The free NA (537 mg), extracted from the concentrated OSPW naphthenate solution as described by Jones et al. (2012), was dissolved in 14 % BF<sub>3</sub>-methanol complex solution (Sigma Aldrich) and heated at 70 °C for 3 hours. The methylated solution was washed with water (Chromasolv® HPLC Grade, Sigma Aldrich) and the methyl esters extracted with hexane (HPLC Grade, Rathburns Chemical Ltd.). The methyl ester solution was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> (≥ 99.0 %, Sigma Aldrich), filtered and evaporated to dryness under N<sub>2</sub> at 40 °C.

The large scale fractionation was performed twice, on two quantities of sample #1. The mass of OSPW NA methyl esters loaded onto the phase in the first fractionation was 296 mg, and 300 mg in the second fractionation. A summary of the fractions for each fractionation is given in Tables S1 and S2.

## TABLES

**Table S-1: Summary of the fractions collected in the first Ag-Ion fractionation of the OSPW NA methyl esters.**

Fraction	Eluent	Mass of eluate / mg
Wash	Hexane	0.4
1	100 % hexane	20.1
2	100 % hexane	76.8
3	100 % hexane	7.4
4	100 % hexane	1.7
5	5 % diethyl ether : 95 % hexane	61.3
6	5 % diethyl ether : 95 % hexane	30.8
7	5 % diethyl ether : 95 % hexane	9.2
8	10 % diethyl ether : 90 % hexane	11.5
9	100 % diethyl ether	29.6
10	100 % methanol	52.1
	Total	300.9
	Total (excluding F10)	248.8

**Table S-2: Summary of the fractions collected in the second Ag-Ion fractionation of the OSPW NA methyl esters.**

Fraction	Eluent	Mass of eluate / mg
Wash	Hexane	0.3
1	100 % hexane	7.7
2	100 % hexane	96.7
3	100 % hexane	16.7
4	100 % hexane	2.1
5	5 % diethyl ether : 95 % hexane	50.0
6	5 % diethyl ether : 95 % hexane	38.2
7	5 % diethyl ether : 95 % hexane	12.9
8	10 % diethyl ether : 90 % hexane	15.1
9	100 % diethyl ether	36.1
10	100 % methanol	222.9
Total		498.4
Total (excluding F10)		275.5

**Table S-3: Summary of the masses and yields for the conversion of the Ag-Ion fractions 2, 5 and 7 of the derivatised OSPW NA and of the underderivatised, unfractionated OSPW NA samples, to hydrocarbons.**

Starting Reactant		Starting mass and yield / mg (approx. percentage yield / %)					
Derivatised (# sample number)	Fraction	LiAlH <sub>4</sub> Reduction		Tosylation		Super-Hydride® Reduction	
		NA methyl esters / mg	Alcohols / mg	Alcohols / mg	Tosylates / mg	Tosylates / mg	Hydrocarbons / mg
Yes (#1)	2	10 <sup>†</sup>	9.8 (104 % <sup>‡</sup> )	9.8	13.3 (82 % <sup>‡</sup> )	12.2	20.7*
Yes (#1)	5	25 <sup>†</sup>	23.0 (97 % <sup>‡</sup> )	23.0	27.9 (77 % <sup>‡</sup> )	27.9	17.2*
Yes (#1)	7	10 <sup>†</sup>	9.1 (96 % <sup>‡</sup> )	9.1	10.5 (74 % <sup>‡</sup> )	10.5	6.7*
No (#2)	Whole	30 <sup>†</sup>	25.0 (88 % <sup>‡</sup> )	25.0	32.3 (78 % <sup>‡</sup> )	32.0	-

<sup>†</sup> approximate masses, as methyl esters

<sup>‡</sup> approximate yield based on average molecular weight of acid methyl esters as 250 g/mol in F2, 286 g/mol in F5, 294 g/mol in F7 and 246 g/mol in the whole underderivatised OSPW NA

\* hydrocarbon product concentrated by N<sub>2</sub> blowdown resulting in evaporative losses; THF and boroxin residue present

- Kuderna-Danish apparatus used for concentration to reduce volatile compound losses, so no weight was recorded

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**Table S-4: Summary of naphthenic acids within OSPW identified as hydrocarbons after reduction of the esters and analysis by GCxGC-MS**

Assigned label	Type	Hydrogen Deficiency of hydrocarbon or NA (z)	Name of hydrocarbon equivalent	Identification
Ad-I	Tricyclic (diamondoid)	-6	1,2-dimethyladamantane	Mass spectral interpretation, Golovkina et al. (1984); mass spectral comparison, Polyakova et al. (1973); GC elution order, Wingert (1992), Wei et al. (2006), Wang et al. (2013); previous assignment of NA in OSPW and comparison of retention position and mass spectra with reference NA, Rowland et al. (2011a), Bowman et al. (2014), Lengger et al. (2013)
Ad-II	Tricyclic (diamondoid)	-6	1-ethyladamantane	
Ad-III	Tricyclic (diamondoid)	-6	cis-2,4-dimethyladamantane	
Ad-IV	Tricyclic (diamondoid)	-6	trans-2,4-dimethyladamantane	
Ad-V	Tricyclic (diamondoid)	-6	2-ethyladamantane	
Ad-VI-VIII, X-XIII, XVII	Tricyclic (diamondoid)	-6	trimethyladamantane isomers	
Ad-IX, XIV-XVI, XVIII-XX	Tricyclic (diamondoid)	-6	ethylmethyladamantane isomers	
bi-I	Bicyclic	-4	1,4-dimethylbicyclo[3.2.1]octane	Mass spectral comparison, Denisov et al. (1977a); GC elution order Piccolo et al. (2010); previous assignment in petroleum NA and comparison of retention position and mass spectra with reference NA, Wilde and Rowland (2015), Wilde et al. (2015)
bi-II	Bicyclic	-4	1,2-dimethylbicyclo[3.3.0]octane	Mass spectral comparison, Denisov et al. (1977c); GC elution order Piccolo et al. (2010); previous assignment of isomers in petroleum NA and comparison of retention position and mass spectra with reference NA, Wilde and Rowland (2015), Wilde et al. (2015)
bi-III	Bicyclic	-4	3-methylbicyclo[4.3.0]nonane	Mass spectral comparison, Denisov et al. (1977b); GC elution order Piccolo et al. (2010); previous assignment of isomers in petroleum NA and comparison of retention position and mass spectra with reference NA, Wilde and Rowland (2015), Wilde et al. (2015)
bi-IV	Bicyclic	-4	2,6-dimethylbicyclo[3.2.1]octane	Mass spectral comparison, Denisov et al. (1977a); GC elution order Piccolo et al. (2010); previous assignment of isomers in petroleum NA, Wilde and

				Rowland (2015) (tentative)
bi-V and VI	Bicyclic	-4	C <sub>10</sub> dimethylbicyclooctane isomers	Mass spectral comparison, Denisov et al. (1977a) (tentative)
tt-I and II	Tricyclic	-6	C <sub>20</sub> tricyclic terpane; cheilanthane isomers	Mass spectral interpretation and mass spectral comparison, Hall and Douglas (1981), Philp (1985), Chicarelli et al. (1988); previous evidence of terpenoid NA in oil sands, Cyr and Strausz (1983)
tt-III and IV	Tricyclic	-6	C <sub>21</sub> tricyclic terpane; cheilanthane isomers	
tt-V	Tricyclic	-6	C <sub>23</sub> tricyclic terpane; cheilanthane isomer	
tt-VI	Tricyclic	-6	C <sub>24</sub> tricyclic terpane; cheilanthane isomer	
diA-I	Pentacyclic	-10	3-methyldiamantane	Previous assignment of NA isomers in OSPW, Rowland et al. (2011b); mass spectral interpretation, Golovkina et al. (1984) and mass spectral comparison, Kuraš and Hála (1970), Musayev et al. (1983); GC elution order, Wingert (1992), Wang et al. (2013) (higher homologues are tentative)
diA-II	Pentacyclic	-10	ethyldiamantane	
diA-III-IX	Pentacyclic	-10	dimethyl- and ethyldiamantane isomers	
diA-X-XVI	Pentacyclic	-10	ethylmethyldiamantane isomers	
diA-XVII-XXV	Pentacyclic	-10	dimethylethyldiamantane isomers	
tAd-I	Tetracyclic	-8	methyl-2,4-cyclopentano-adamantane	Mass spectral interpretation and evidence of corresponding NA in OSPW, Petrov (1987), Vorob'eva et al. (1986) (higher homologues are tentative)
tAd-II and III	Tetracyclic	-8	ethyl-2,4-cyclopentano-adamantane isomers	
tAd-IV	Tetracyclic	-8	dimethyl-cyclopentano-adamantane	
tAd-V	Tetracyclic	-8	ethylmethyl-cyclopentano-adamantane	
tAd-VI	Tetracyclic	-8	trimethyl-cyclopentano-adamantane	
tAd-VII-IX	Tetracyclic	-8	C <sub>16-18</sub> alkylcyclopentano-adamantane isomers	
ma-I-IV	Monocyclic monoaromatic	-8	C <sub>16-18</sub> alkylbenzene isomers	Mass spectral interpretation and comparison, Larter et al. (1981), Sinninghe Damsté et al. (1988), Ji-Zhou et al. (1993); evidence of corresponding NA in OSPW
mb-I-VI	Bicyclic monoaromatic	-10	C <sub>14-19</sub> alkylindane and tetralin isomers	
tm-I	Tricyclic monoaromatic	-12	13-methyl-14-ethylpodocarpa-8,11,13-triene	Mass spectral comparison, Azevedo et al. (1990), Azevedo et al. (1992) and NIST MS library; previous assignment of monoaromatic terpenoid NA in tasmanite, Azevedo et al. (1994)
dbt-I	Sulphur-containing tricyclic diaromatic	-18	4-isobutyldibenzothiophene	Comparison of retention position with synthetic reference hydrocarbon, Wilde (2015); mass spectral interpretation and mass spectral comparison, Andersson et al. (2001), Bobinger et al. (1999), (Andersson and Schade, 2004), Li et al. (2014); previous assignment of NA

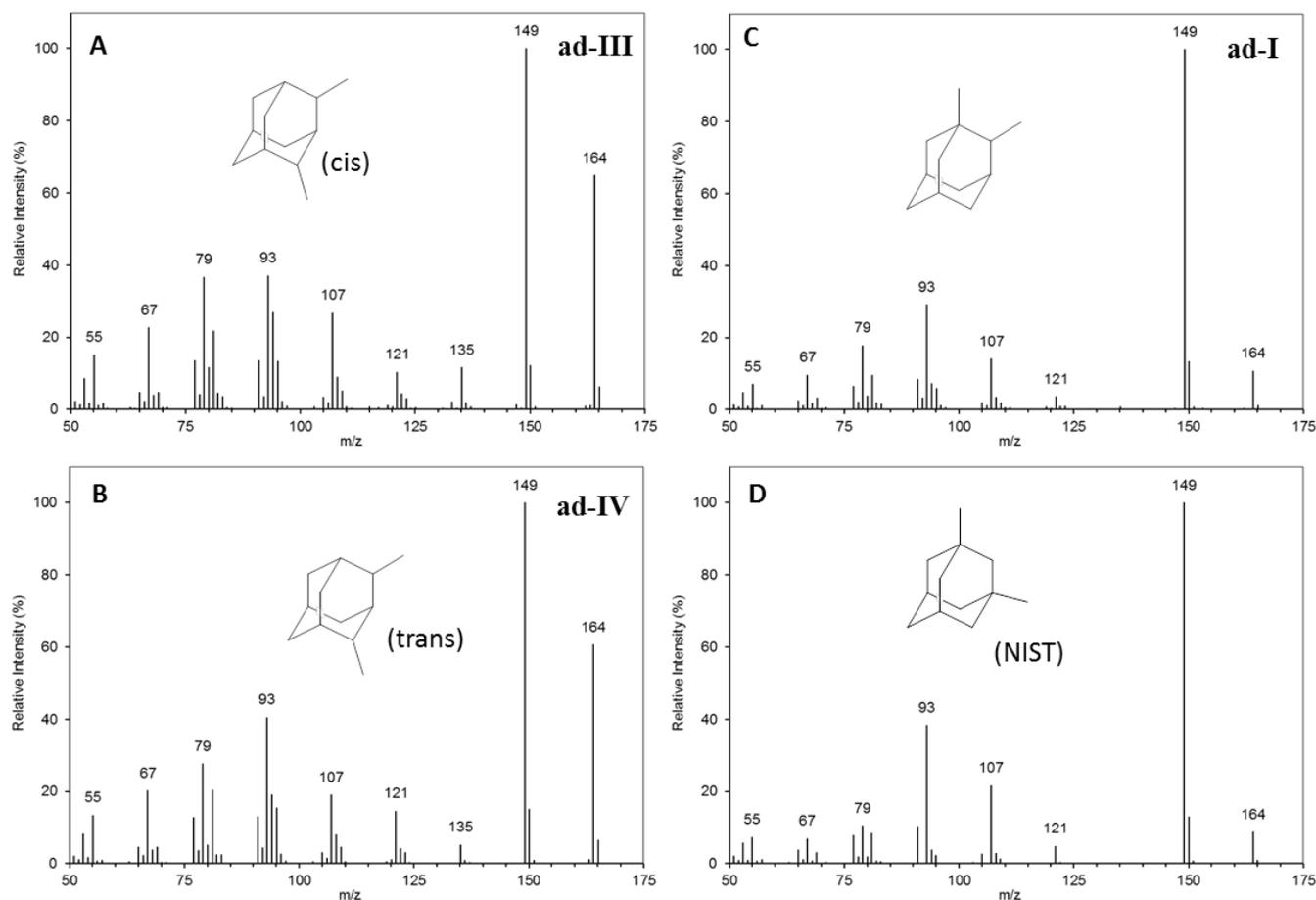
Please note: This is an accepted, pre-publication, manuscript. Readers are advised to consult the final, published version: doi: [10.1016/j.orggeochem.2017.09.004](https://doi.org/10.1016/j.orggeochem.2017.09.004)

				isomers in OSPW, West et al. (2014)
dbt-II and III	Sulphur-containing tricyclic diaromatic	-18	methyl-isobutyldibenzothiophene isomers	Mass spectral interpretation and mass spectral comparison, Andersson et al. (2001), Bobinger et al. (1999), Andersson and Schade (2004), Li et al. (2014); previous assignment of NA isomers in OSPW, West et al. (2014)
dbt-IV and V	Sulphur-containing tricyclic diaromatic	-18	dimethyl-isobutyldibenzothiophene	
nat-I-V	Sulphur-containing tricyclic diaromatic	-16	alkyl 2H-naphtho[1,8-bc]thiophenes isomers	Mass spectral interpretation and comparison, (Porter, 1985), (Hawthone and Porter, 1968) and NIST MS library

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## FIGURES



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41 Figure S-1. Mass spectra of isomers ad-I, III and IV (labels refer to components in EIC in Figure 1 in main text) assigned as  
42 dimethyladamantanes including (A and B) two isomers of 2,4-dimethyladamantane (III and IV) and (C) 1,2-  
43 dimethyladamantane (I) by comparison of the known GC elution order of alkyl adamantanes relative to 1- and 2-  
44 ethyladamantane (II and V) and by comparison with (D) the reference mass spectrum of 1,3-dimethyladamantane  
45 (Polyakova et al., 1973; Wingert, 1992; Wang et al., 2013).

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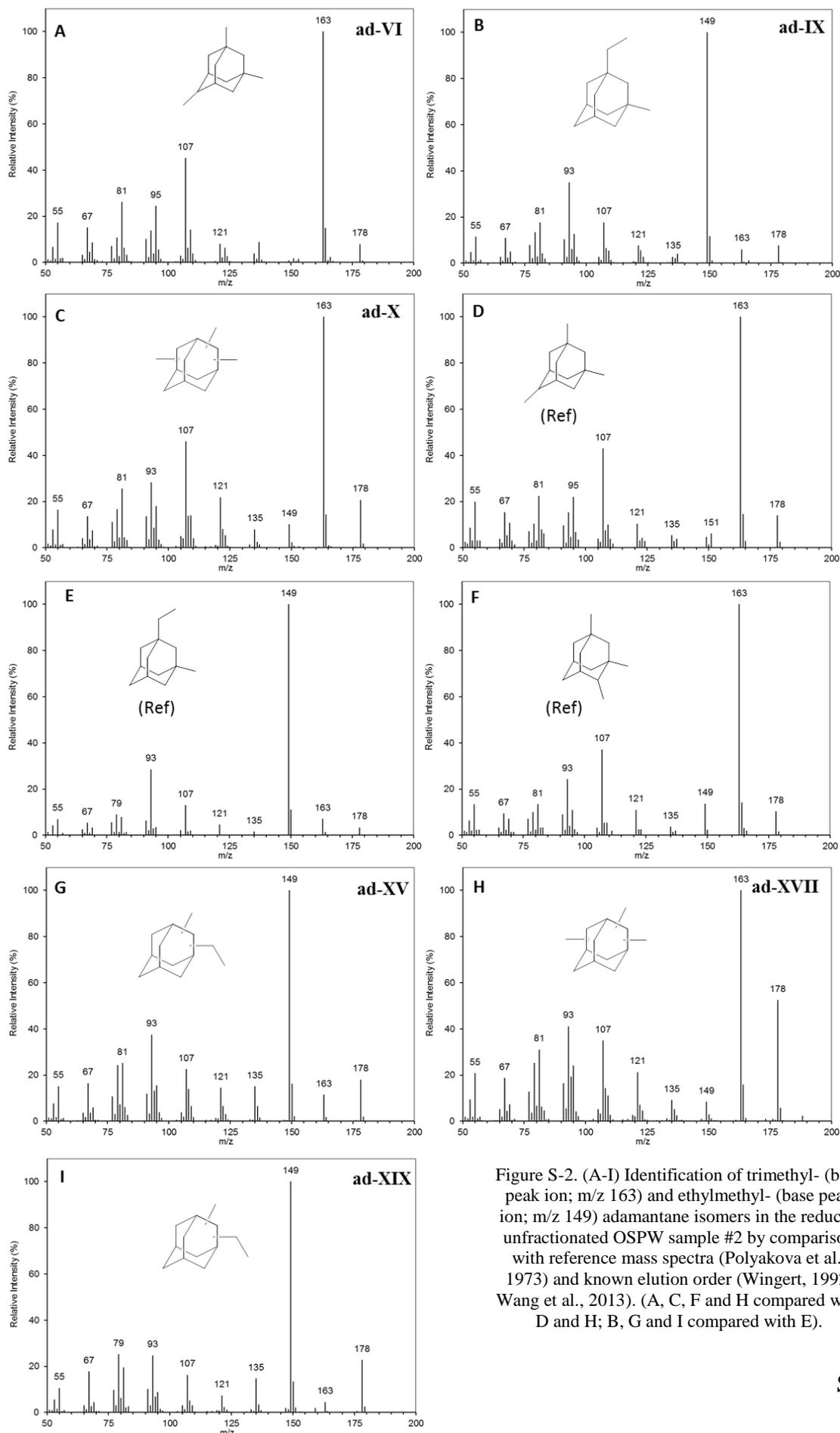
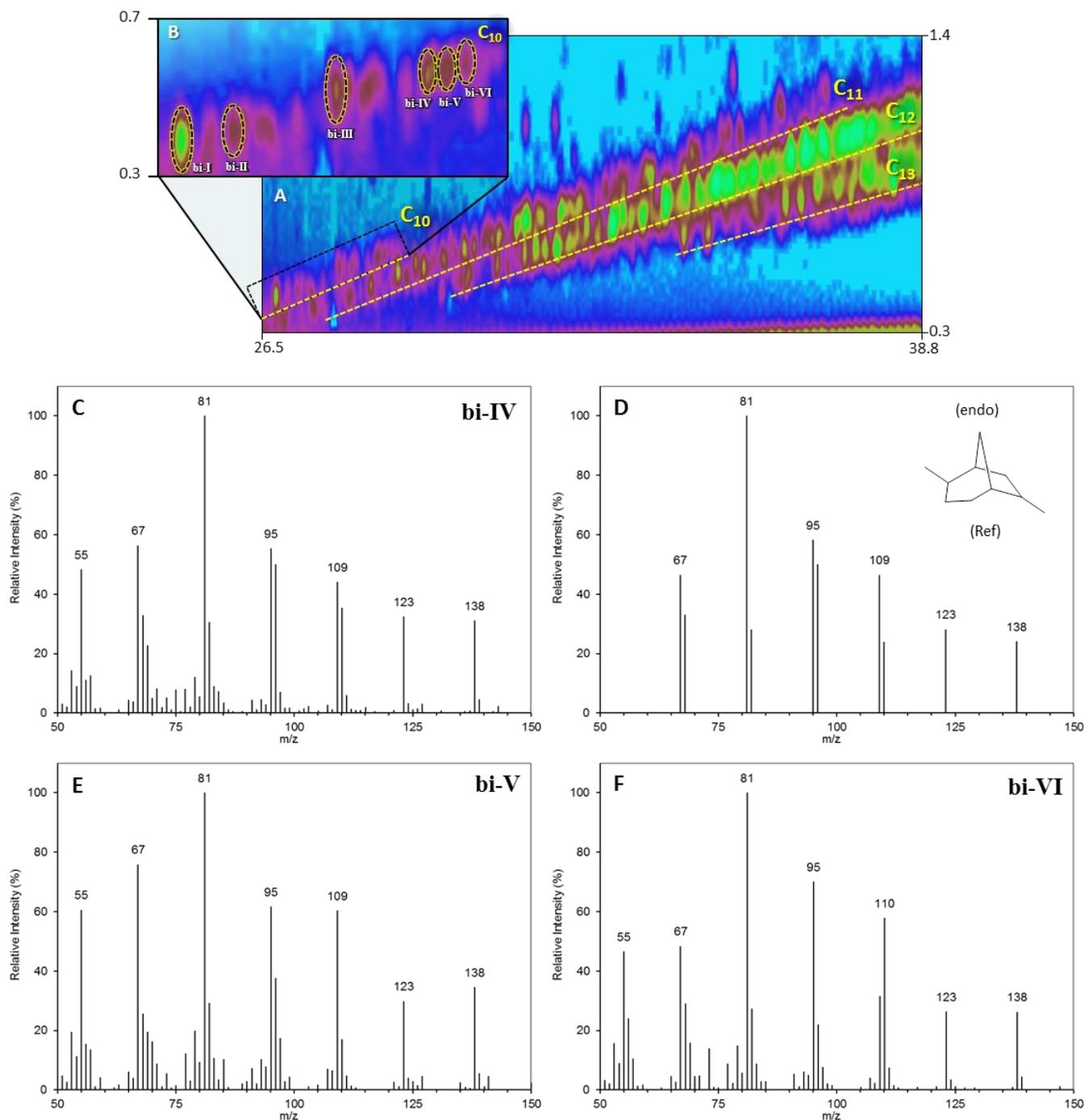
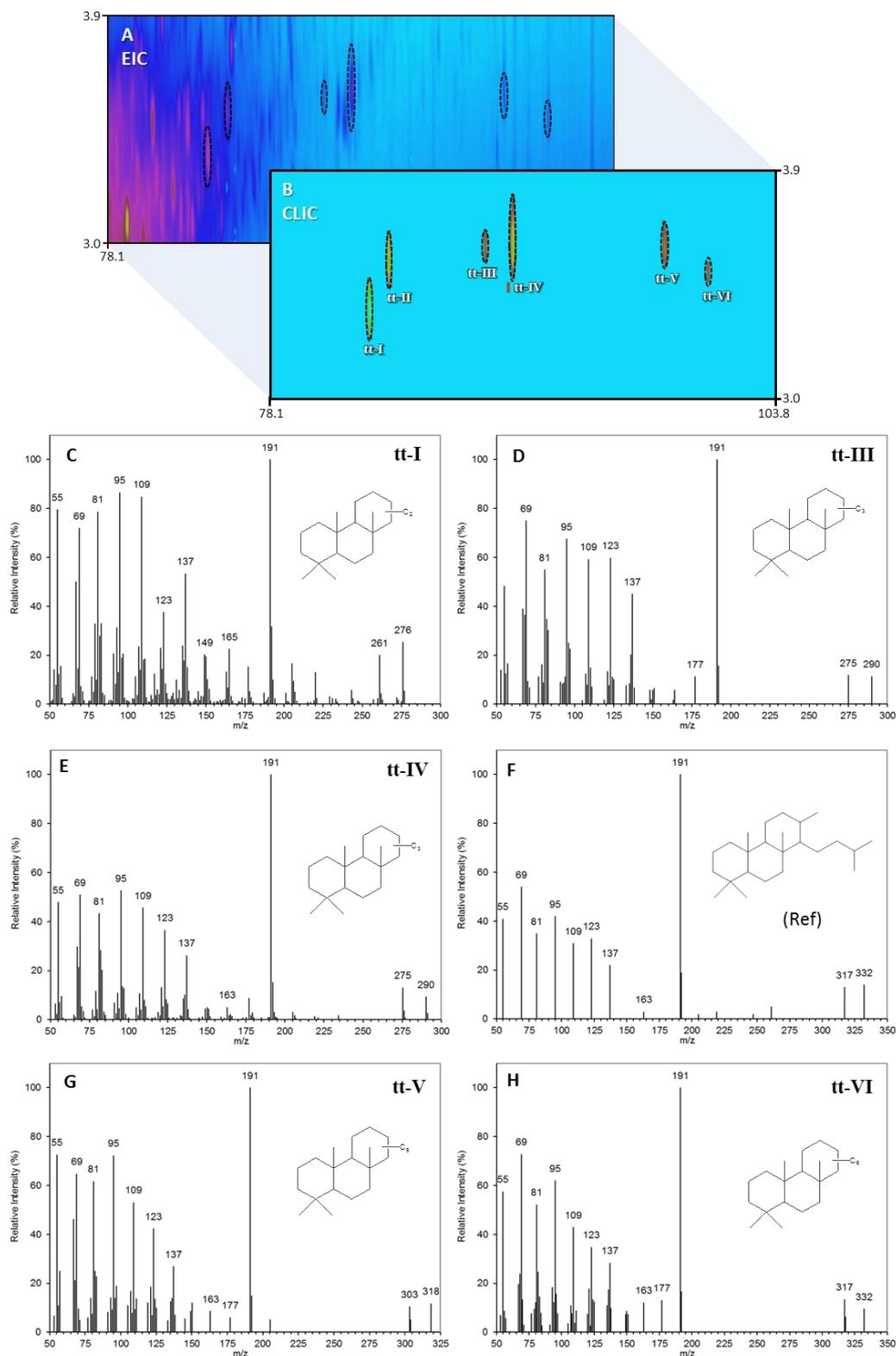


Figure S-2. (A-I) Identification of trimethyl- (base peak ion; m/z 163) and ethylmethyl- (base peak ion; m/z 149) adamantane isomers in the reduced unfractionated OSPW sample #2 by comparison with reference mass spectra (Polyakova et al., 1973) and known elution order (Wingert, 1992; Wang et al., 2013). (A, C, F and H compared with D and H; B, G and I compared with E).



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50 Figure S-3. Mass spectra of C<sub>10</sub> bicyclanes (bi-IV to VI) in the reduced unfractionated NA (sample #2). (A) Isomer bi-IV  
51 assigned after comparison with (B) the reference mass spectrum of endo-endo-2,6-dimethylbicyclo[3.2.1]octane. (C and D)  
52 Mass spectra of isomers bi-V and VI which did not match any reference spectra and were significantly different to those  
53 within reduced petroleum-derived acids previously reported (Wilde and Rowland, 2015).



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55 Figure S-4. (A) EIC (m/z 191) and (B) CLIC expression chromatogram revealing series of isomers assigned as (C-H) C<sub>20</sub> (tt-  
 56 I and II), C<sub>21</sub> (tt-III and -IV), C<sub>23</sub> (tt-V) and C<sub>24</sub> (tt-VI) tricyclic terpanes by comparison with reference mass spectra (Hall  
 57 and Douglas, 1981; Cyr and Strausz, 1983; Philp, 1985; Chicarelli et al., 1988). (All mass spectra share similar  
 58 fragmentation pattern to reference mass spectrum F, particularly H and F).

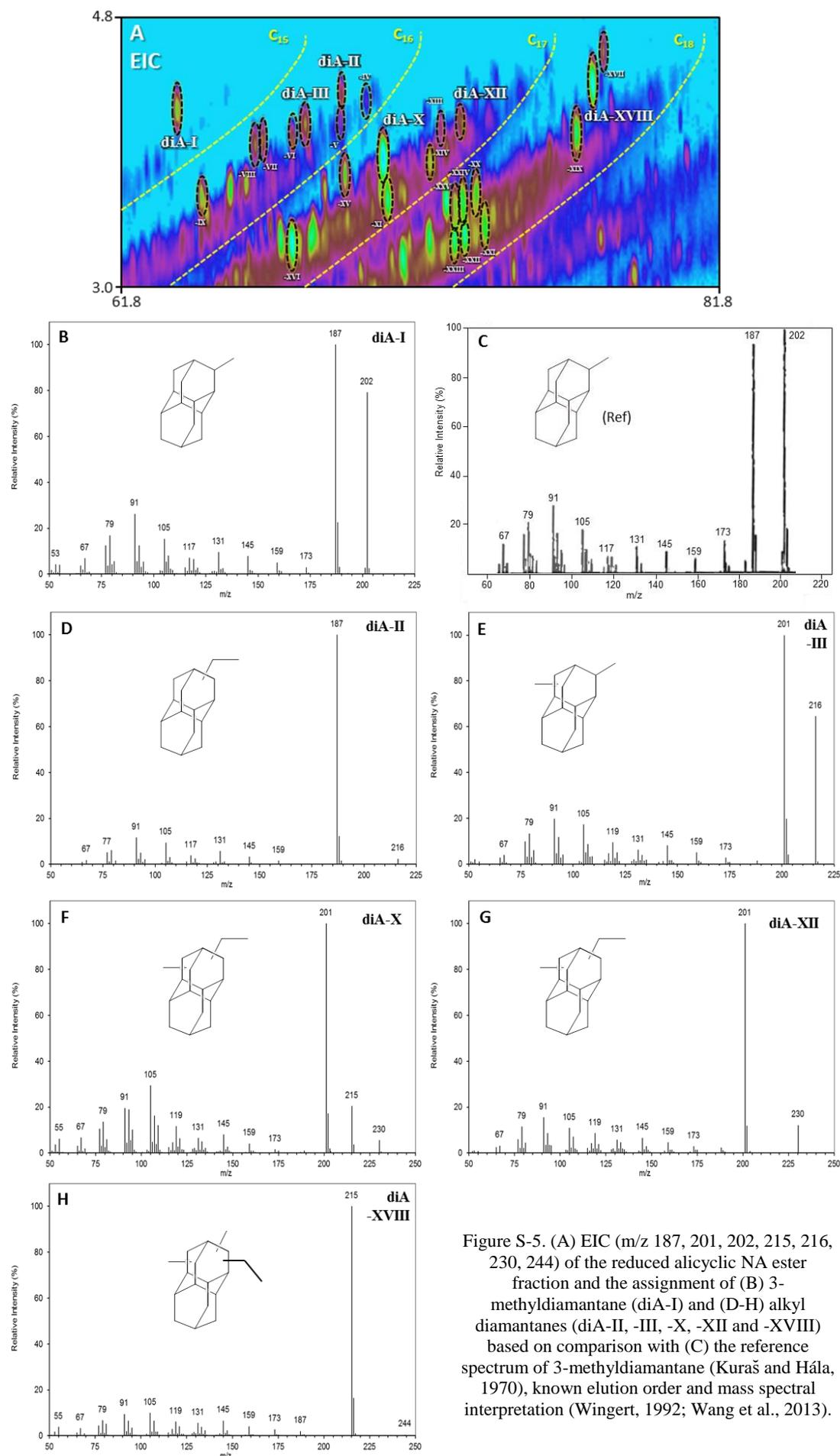
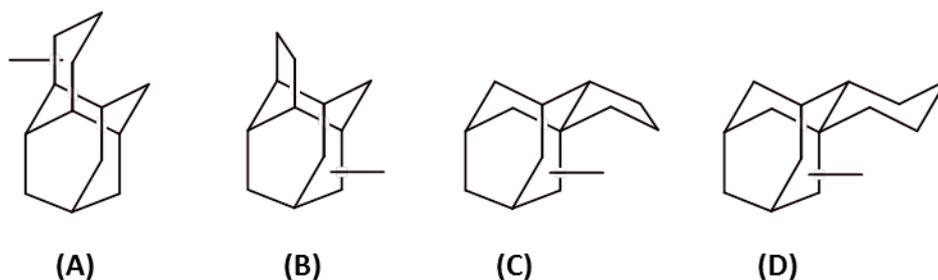


Figure S-5. (A) EIC (m/z 187, 201, 202, 215, 216, 230, 244) of the reduced alicyclic NA ester fraction and the assignment of (B) 3-methyldiamantane (diA-I) and (D-H) alkyl diamantanes (diA-II, -III, -X, -XII and -XVIII) based on comparison with (C) the reference spectrum of 3-methyldiamantane (Kuraš and Hála, 1970), known elution order and mass spectral interpretation (Wingert, 1992; Wang et al., 2013).

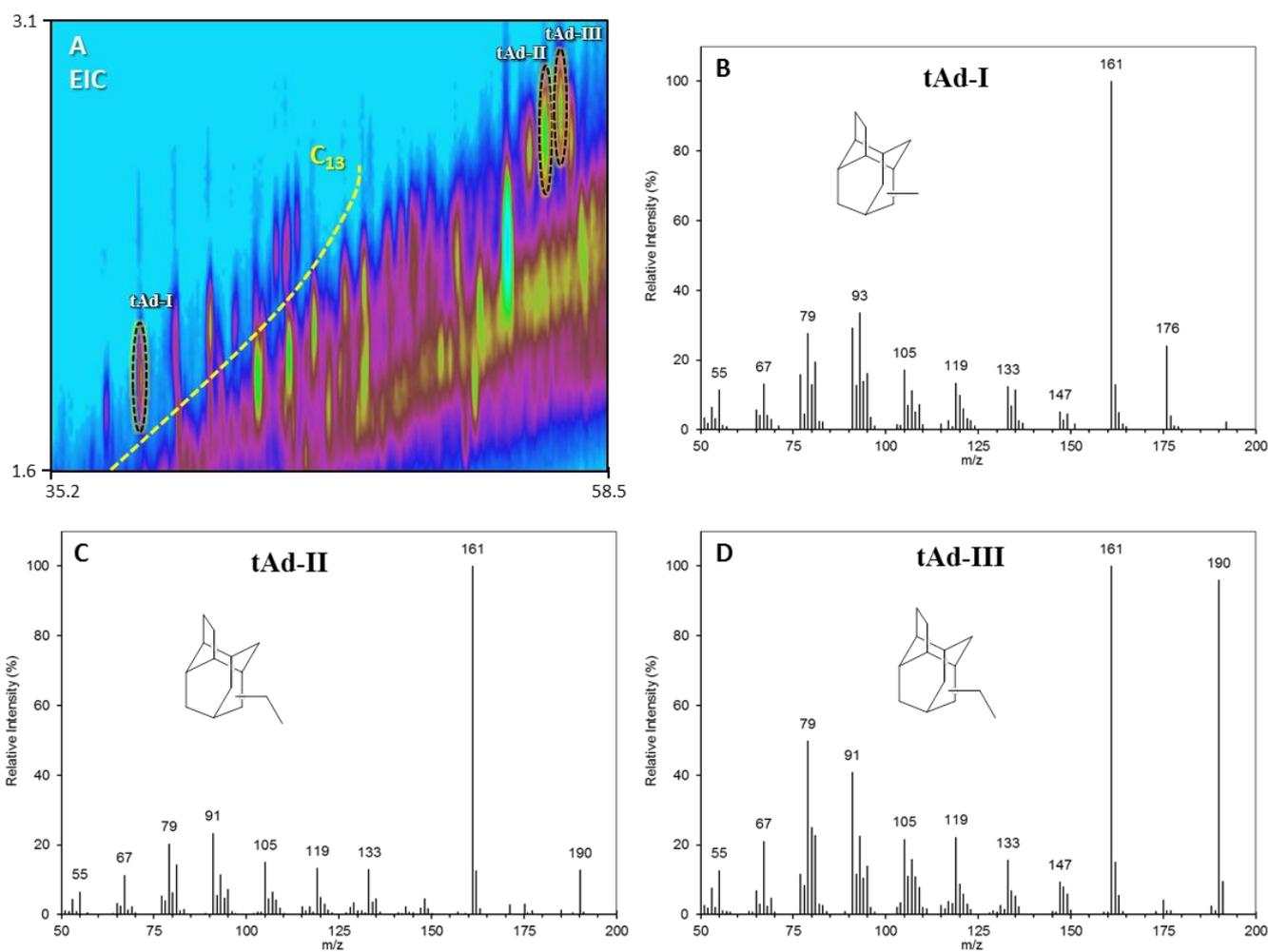


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61 Figure S-6. Examples of substituted tetracyclic diamondoid compounds showing the structure of the skeletal core, including  
62 (A) 2,4-cyclohexano-adamantane (tetracyclic ring-opened diamantane), (B) 2,4-cyclopentano-adamantane, (C) 1,2-  
63 cyclopentano-adamantane and (D) 1,2-cyclohexano-adamantane.

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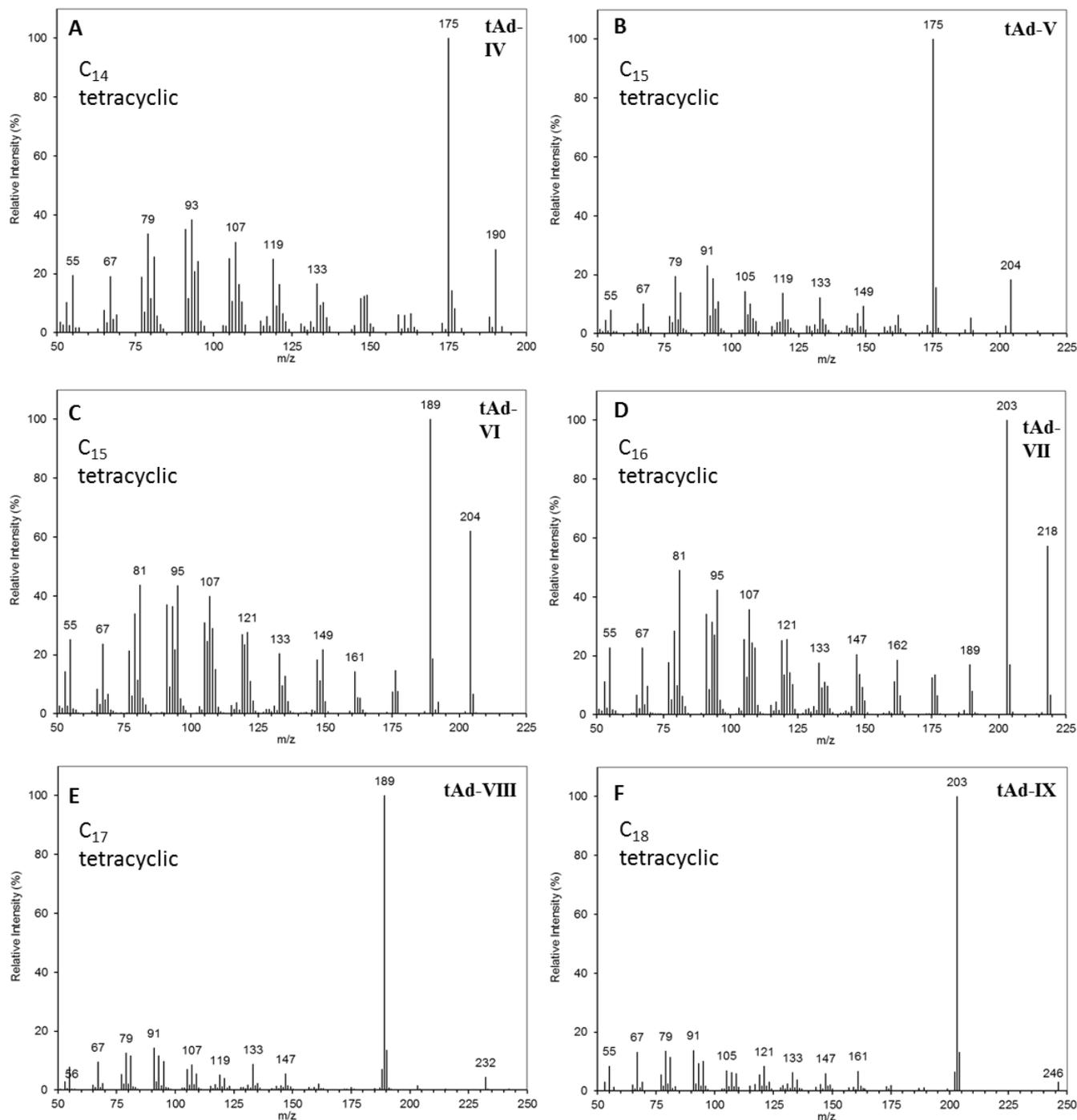


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67 Figure S-7. (A) EIC (m/z 161, 175, 176, 189, 190, 203, 217) of the reduced sample #2, showing components tAd-1 to -III  
68 with (B-D) mass spectra containing molecular ions corresponding to C<sub>13</sub> and C<sub>14</sub> tetracyclic hydrocarbons, tentatively  
69 assigned as alkyl 2,4-cyclopentano-adamantanes.

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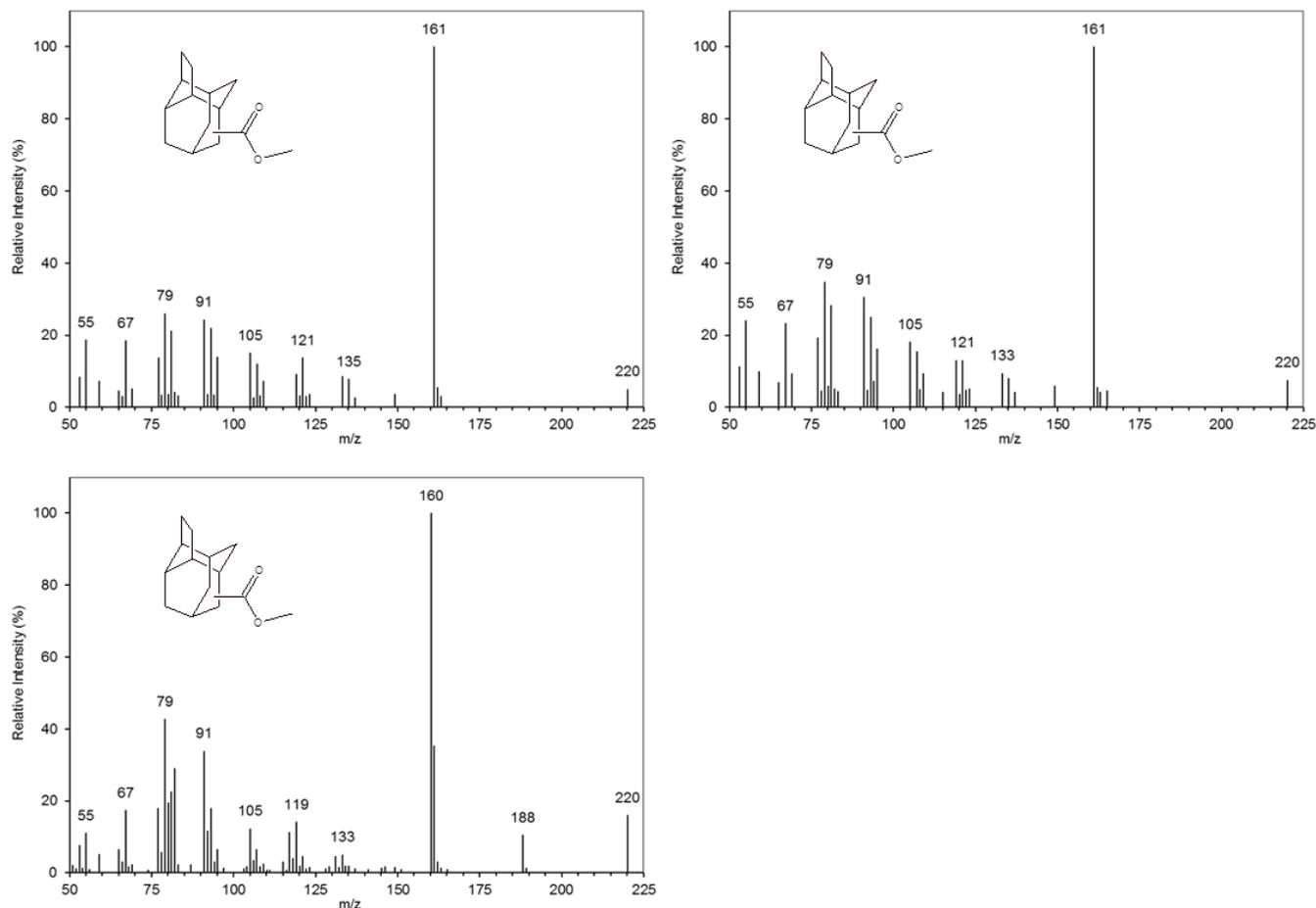
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Figure S-8. (A-F) Mass spectra of  $C_{14-18}$  alkyl tetracyclic hydrocarbons (isomers tAd-IV to tAd-IX) in the reduced sample #2, postulated to possess adamantanoid structures (e.g. Figure S-6; A-D).



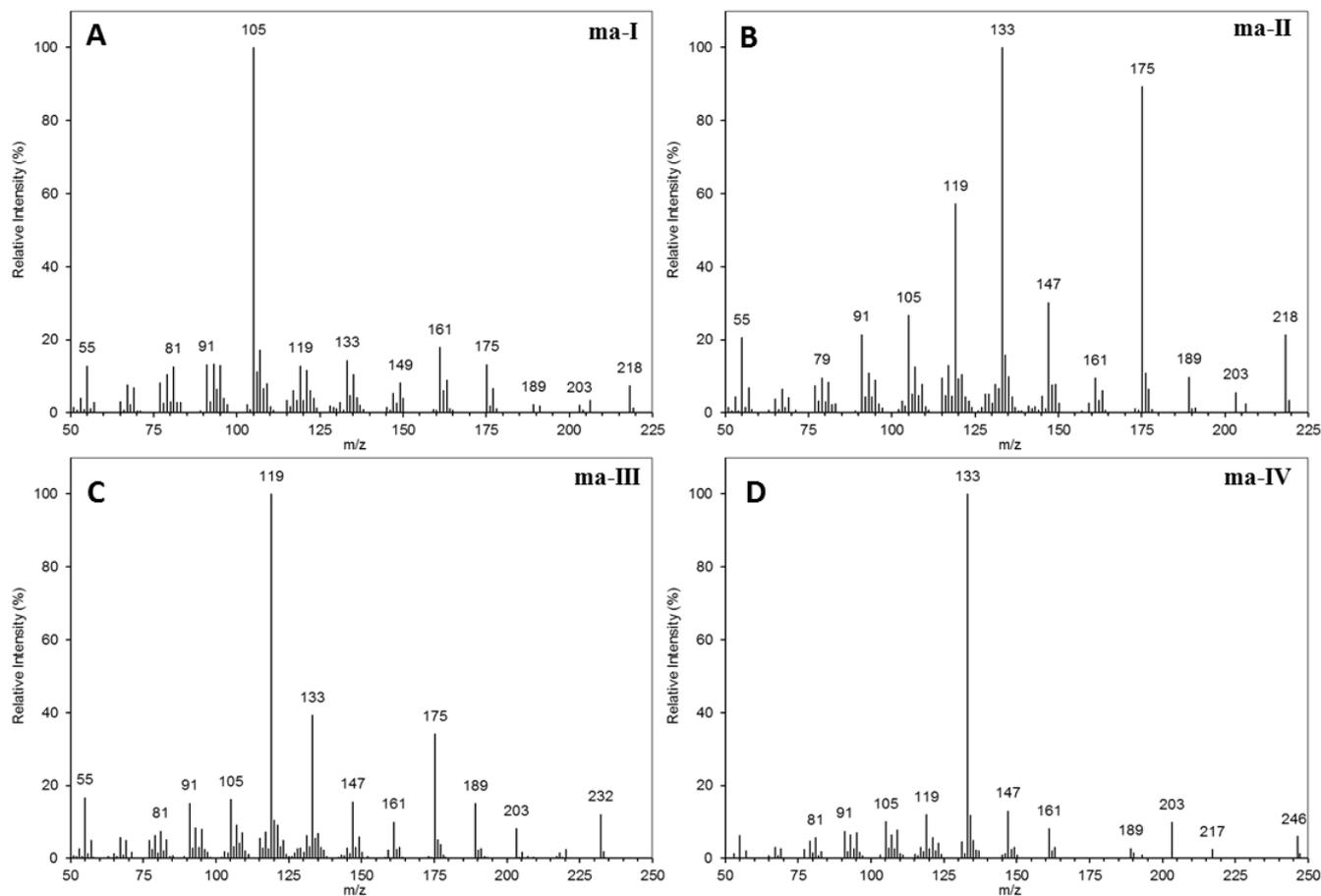
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Figure S-9. Electron ionisation mass spectra of components in sample #2 NA methyl esters tentatively assigned as cyclopentano-adamantane acids after examination of the mass spectra of the corresponding hydrocarbons.



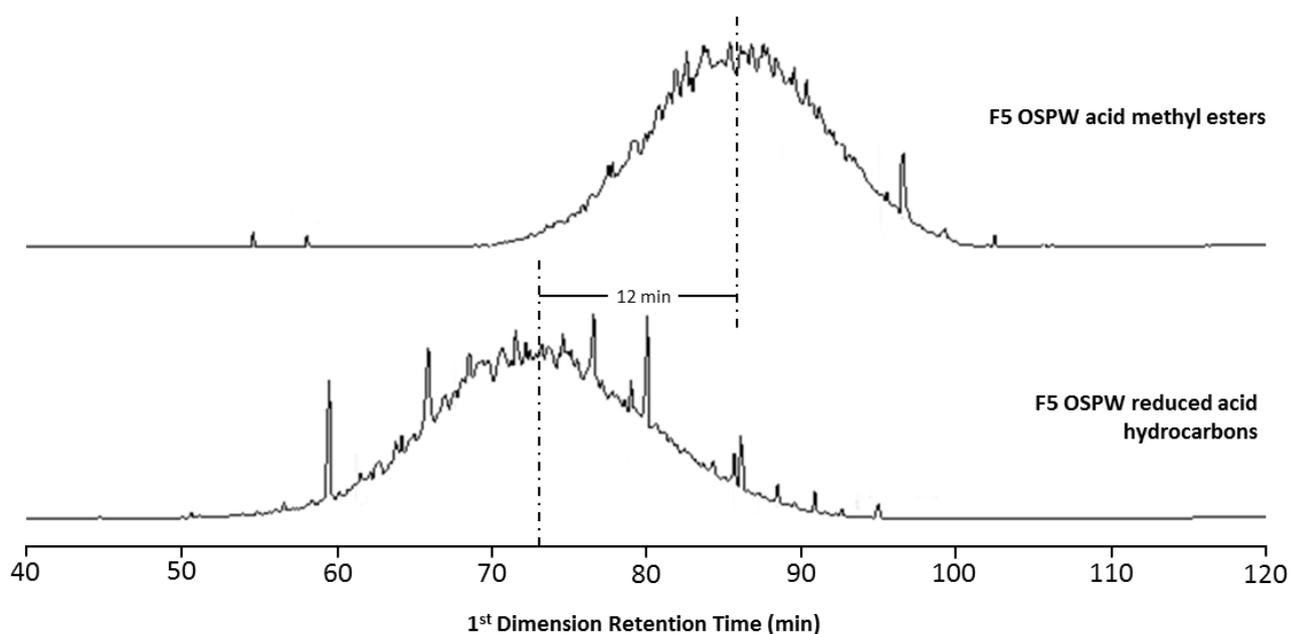
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Figure S-10. (A-D) Example mass spectra of components assigned as  $C_{16-18}$  alkylbenzenes within the reduced aromatic fraction of sample #1.

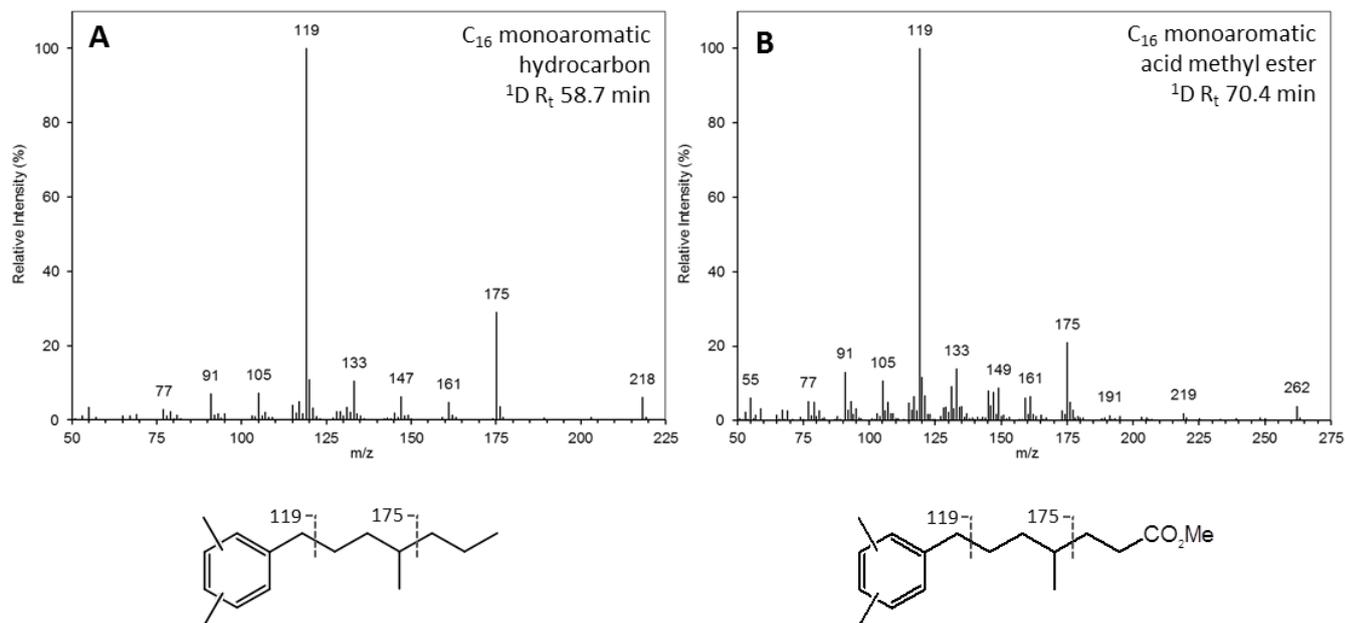


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Figure S-11. Comparison of the GC-MS TIC chromatograms before (top) and after (bottom) reduction of the 'aromatic' fraction of sample #1 acid methyl esters, to the corresponding hydrocarbons.

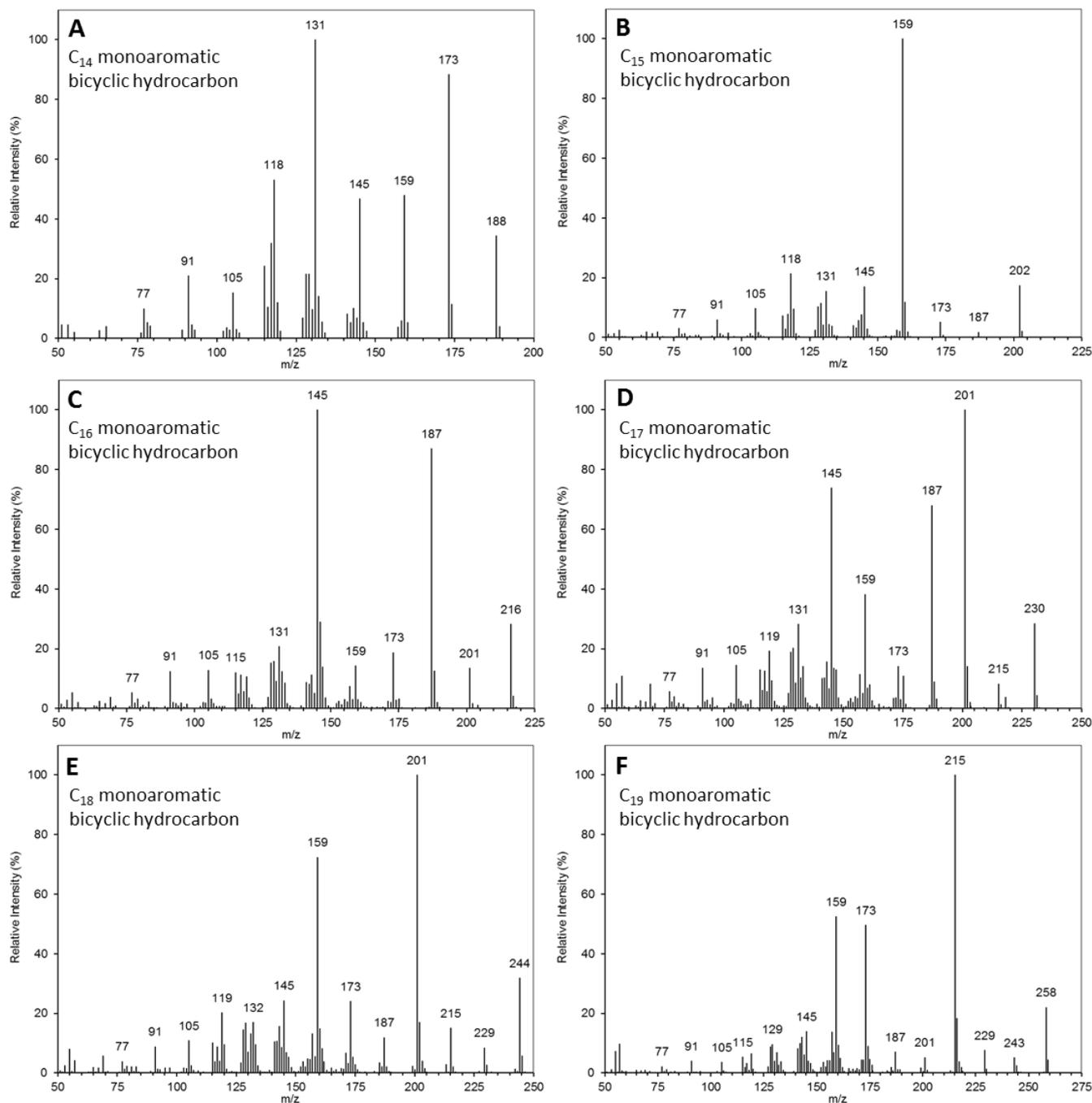


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89 Figure S-12. (A) Mass spectrum of a C<sub>16</sub> monoaromatic hydrocarbon in the reduced aromatic fraction of sample #1, assigned  
90 as a dimethyl branched alkylbenzene, based on comparison with reference spectra and mass spectral interpretation and (B)  
91 the mass spectrum of a C<sub>16</sub> monoaromatic acid methyl ester, assigned as the corresponding alkylbenzene acid methyl ester  
92 before reduction of the aromatic fraction. Structures given are speculative, to demonstrate key fragment ions observed.

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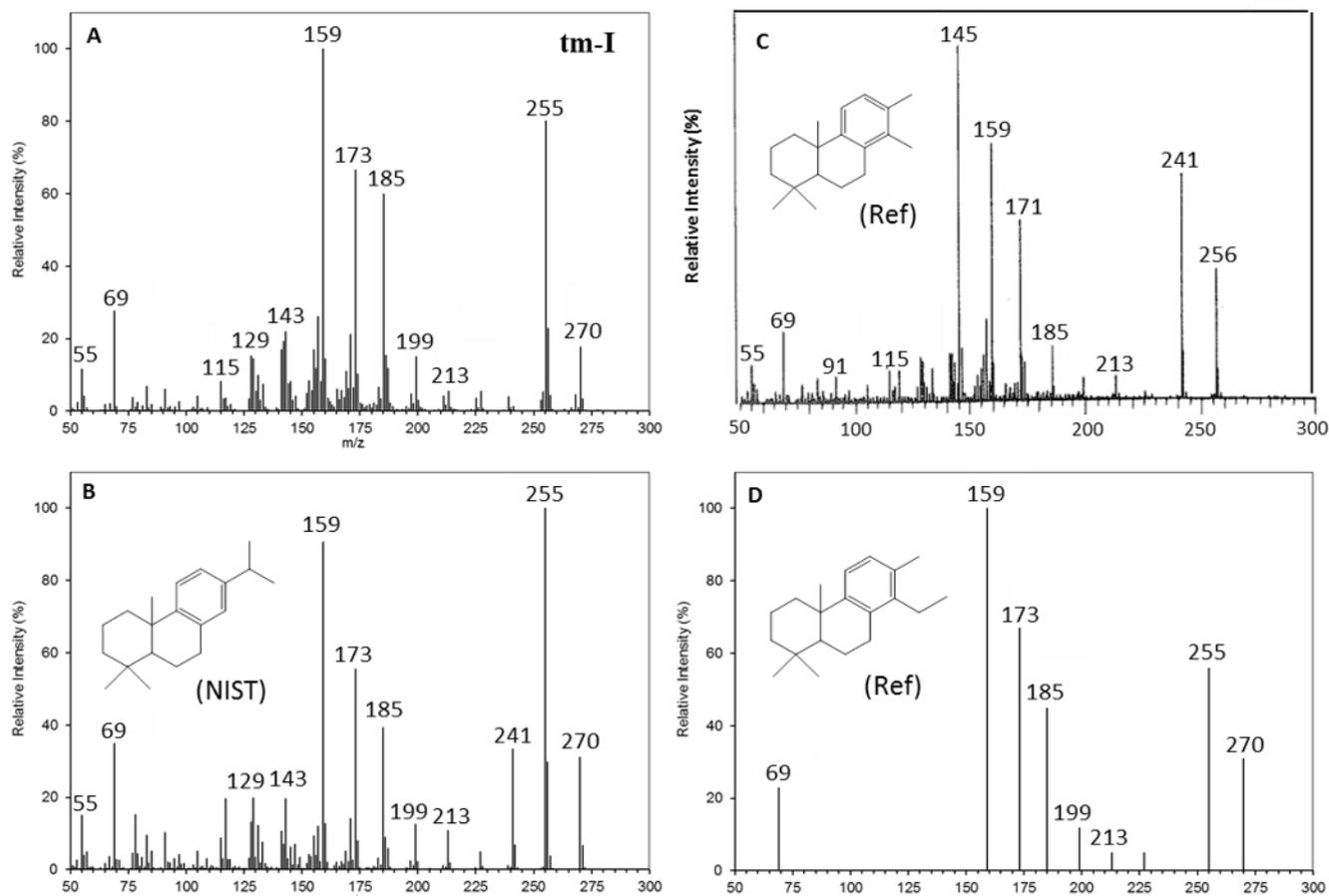
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Figure S-13. (A-F) Mass spectra of C<sub>14-19</sub> monoaromatic bicyclic hydrocarbons tentatively assigned based on mass spectral comparison and interpretation.

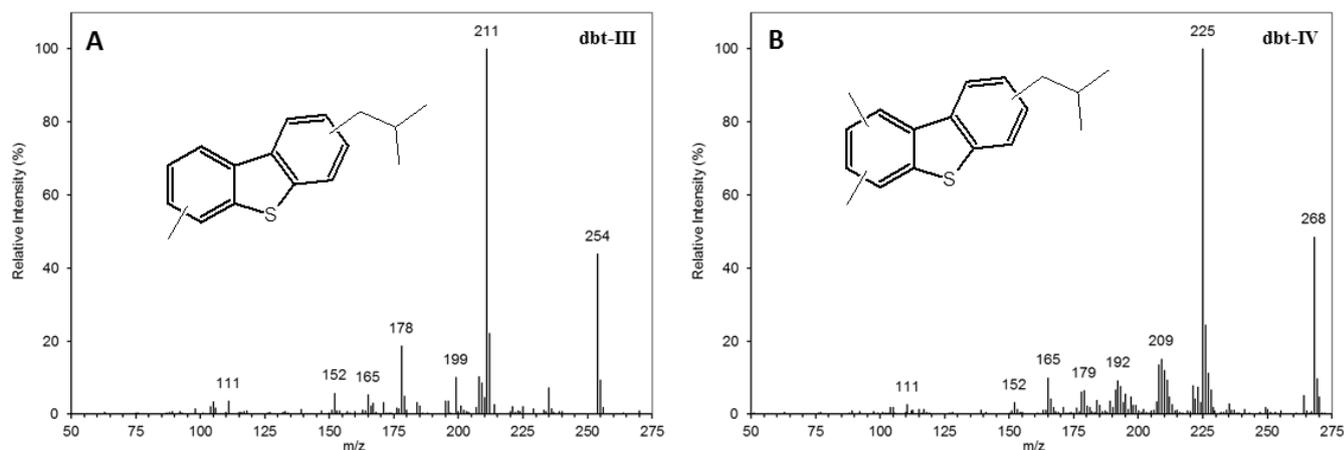


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103 Figure S-14. (A) Mass spectrum of isomer tm-I, a C<sub>20</sub> tricyclic monoaromatic hydrocarbon assigned as 13-methyl-14-  
104 ethylpodocarpa-8,11,13-triene after comparison with the mass spectra of (B) dehydroabietane plotted from the NIST MS  
105 Library, (C) 13,14-dimethylpodocarpa-8,11,13-triene reimagined from the spectrum reported by Azevedo et al. (1992) and (D)  
106 13-methyl-14-ethylpodocarpa-8,11,13-triene replotted from the tabulated values reported by Azevedo et al. (1990).

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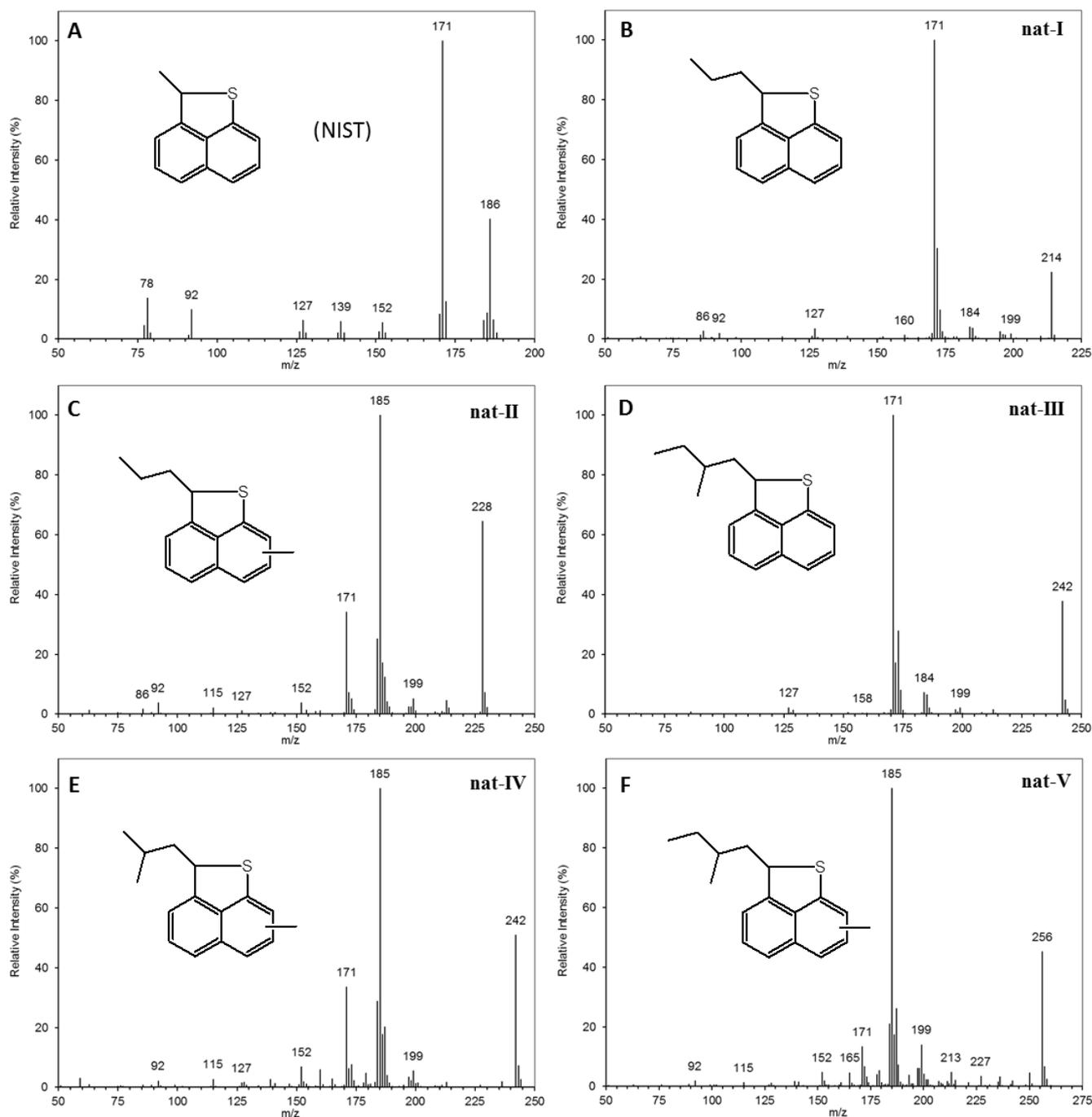
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Figure S-15. (A and B) Assignment of dbt-III and -IV as methyl- and dimethyl- isobutyldibenzothiophenes.

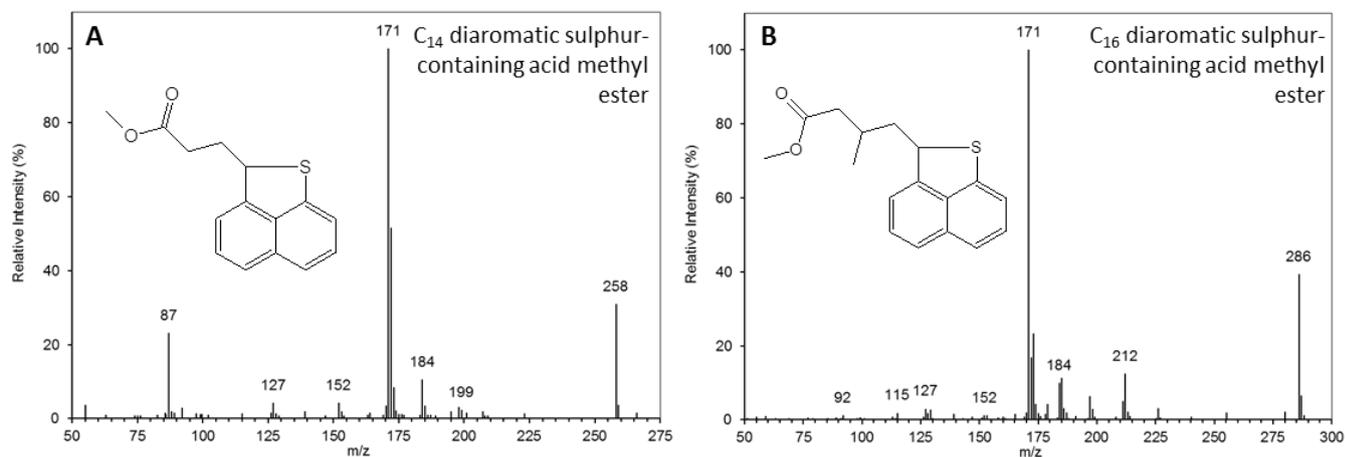


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Figure S-16. Mass spectra of a series of isomers (nat-I to -V) in the reduced 'aromatic, sulphur' fraction of sample #1, tentatively assigned, after comparison with (A) the NIST spectrum of 2-methyl-2H-naphtho[1,8-bc]thiophene and their retention positions relative to authentic 4-propyl- and isobutyl- dibenzothiophene, as (B-F) 2-alkyl (C3-5) substituted 2H-naphtho[1,8-bc]thiophenes and methyl 2H-naphtho[1,8-bc]thiophenes.

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123 Figure S-17. (A and B) Example mass spectra of a C<sub>14</sub> and C<sub>16</sub> acid methyl ester in the 'aromatic, sulphur' fraction of sample  
124 #1, with molecular ions and retention positions consistent with condensed tricyclic, diaromatic sulphur-containing acid  
125 methyl esters, tentatively assigned as naphtho[1,8-bc]thiophene acids.

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Please note: This is an accepted, pre-publication, manuscript. Readers are advised to consult the final, published version: doi: [10.1016/j.orggeochem.2017.09.004](https://doi.org/10.1016/j.orggeochem.2017.09.004)

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