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DIAMONDROID DIACIDS (O_4 SPECIES) IN OIL SANDS PROCESS AFFECTED WATER

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Abstract

RATIONALE: As a by-product of oil sands extraction, large volumes of oil sands process water (OSPW) are generated, which are contaminated with a large range of water-soluble organic compounds. The acids are thought to be derived from hydrocarbons via natural biodegradation pathways such as α - and β -oxidation of alkyl substituents, which could produce mono- and diacids, for example. However, while several monoacids (O_2 species) have been identified, the presence of diacids (i.e. O_4 species) has only been deduced from results obtained via Fourier transform infrared (FTIR) spectroscopy, Fourier transform ion cyclotron resonance high-resolution mass spectrometry (FTICR-HRMS) and nuclear magnetic resonance (1H -NMR) spectroscopy and the structures have never been confirmed.

METHODS: An extract of an OSPW from a Canadian tailings pond was analysed and the retention times and the electron ionization mass spectra of some analytes were compared with those of bis-methyl esters of authentic diacids by gas chromatography \times gas chromatography/time-of-flight mass spectrometry (GCxGC/TOFMS) in nominal and accurate mass configurations.

RESULTS: Two diamondoid diacids (3-carboxymethyladamantane-1-carboxylic acid and adamantane-1,3-dicarboxylic acid) were firmly identified as their bis-methyl esters by retention time and mass spectral matching and several other structural isomers were more tentatively assigned. Diacids have substantially increased polarity over the hydrocarbon and monoacid species from which they probably derive: as late members of biodegradation processes they may be useful indicators of weathering and ageing, not only of OSPW, but potentially of crude oil residues more generally.

CONCLUSIONS: Structures of O_4 species in OSPW have been identified. This confirms pathways of microbial biodegradation, which were only postulated previously, and may be a further indication that remediation of OSPW toxicity can occur by natural microbial action. The presence and abundance of these diacids might therefore be useful as a measure of biodegradation and weathering.

INTRODUCTION

Exploitation of the oil sands of the Canadian Athabasca region involves using large volumes of water, which becomes contaminated with water-soluble compounds during the extraction process. This oil sands process water (OSPW) is stored in large tailings ponds, due to a non-release policy, since concerns exist about its toxicity to aquatic and terrestrial life. Concerns have been raised especially over the effects of naphthenic acids, components of the acid-extractable watersoluble fraction, which have been shown to have some toxic effects on, in particular, fish, plankton, trees and flowering plants.^[1–4] Identification of some individual naphthenic acids in these highly complex polar mixtures has been undertaken mainly by deployment of gas chromatography \times gas chromatography/time-of-flight mass spectrometry (GCxGC/TOFMS^[5–9]). For example, this method revealed the presence of polycyclic diamondoid acids possessing an adamantane or diamantane core and suggested the use of the varying distributions of these in environmental profiling of OSPW from different industrial pro-

ducers.^[7,10] When the toxicities of fractions of naphthenic acids of increasing molecular weight (MW) were tested, it appeared that higher MW compounds did not exhibit a higher toxicity, contrary to what is usually observed.^[3,4] The reason for this was not understood, until Fourier transform ion cyclotron resonance high-resolution mass spectrometry (FTICR/HRMS),^[11–13] as well as Fourier transform infrared (FTIR) spectroscopy and 1H -nuclear magnetic resonance (NMR) spectroscopy analyses^[14] of different MW fractions of naphthenic acids from OSPW indicated the presence of some higher oxidized compounds. Compounds with four oxygen atoms (O_4 species) were proposed to be diacids and suggested to be products of the biodegradation of alkylated monoacid O_2 species. Significantly, such diacids, particularly when bis-derivatized, would have higher MWs than the corresponding monoacids, yet would be more water-soluble and less toxic. This agrees with the observed decrease in toxicity with increasing MW. Suggested biodegradation pathways explaining the origins of the acids included β -oxidation or combined α - and β -oxidation, depending on whether the oxidised alkyl chain was of even or odd carbon

number.^[15] However, none of the previous studies could suggest structures for the diacids.

In this work, we report the structures of several adamantane diacids in OSPW obtained in 2011 from West In-Pit, a Canadian oil sands tailings pond (Syncrude Ltd). By using methylated authentic adamantane diacids, the retention times and mass spectra could be compared with those of resolved peaks in the sample. The confirmation of the presence and structures of adamantane diacids in oil sands process water not only supports some of the reveals promising indicator compounds for helping to determine the extent of biodegradation and hence the expected toxicity of oil sands process waters of different ages or which are at different stages of remediation.

EXPERIMENTAL

Adamantane-1,3-dicarboxylic acid, 3-carboxymethyladamantane-1-carboxylic acid and noradamantane carboxylic acid were purchased from Sigma-Aldrich (Gillingham, UK). The OSPW sample was obtained from the West In-Pit tailings pond of Syncrude Ltd, Canada, by Environment Canada on 21-11-2011. Samples were filtered through a 0.2 µm filter cartridge to remove suspended solids, acidified to pH 2 and cleaned using 200 mg ENV+ solid-phase extraction (SPE) cartridges (Biotage, Charlotte, NC, USA), followed by elution with 10 mL of acetonitrile, and an aliquot was used for esterification. The pure acids and the environmental extracts were esterified (converted into methyl esters) by reaction with BF₃-methanol complex (Sigma-Aldrich) at 70°C for 20 min. Deuterio-methylated standards were obtained by conducting the same derivatization with BF₃-trideuteriomethanol complex (Sigma-Aldrich). OSPW was also spiked with a deuterated internal standard, noradamantane carboxylic acid d₃ methyl ester, prior to analysis to facilitate retention time comparisons between the OSPW sample mixture and mixtures of reference compounds.

Comprehensive gas chromatography/time-of-flight mass spectrometry (GCxGC/TOFMS) with electron ionization (EI) analyses were conducted using a model 7890A gas chromatograph (Agilent Technologies, Wilmington, DE, USA) fitted with a ZX2 GCxGC cryogenic modulator (Zoex, Houston, TX, USA) interfaced with a BenchTOFdx™ time-of-flight mass spectrometer (Almsco International, Llantrisant, UK) at a scan speed of 50 Hz, i.e. 50 spectra were acquired per second. The first-dimension column was a 5% phenylmethylpolysiloxane HP-5 ms (30 m×0.25 mm×0.25 µm; Agilent Technologies) and the second-dimension column was a 50% phenyl polysilphenylene siloxane BPX50 (3 m×0.10 mm×0.10 µm; SGE, Melbourne, Australia). Helium was used as the carrier gas and the flow rate was 2 mL/min. Samples (1 µL) were injected at 280 °C splitless. The GC conditions were optimized in order to obtain sufficient separation of the peaks eluting at higher *R*_{t1} and *R*_{t2} retention times with a run time of 131 min at a low-temperature ramp of 2 °C min⁻¹. The oven was programmed from 80°C (hold for 1 min), heated to 340 °C at 2 °C min⁻¹ and then held for 10 min. The secondary column was heated at a 10 °C offset, and the hot jet at a 60 °C offset. The modulation period was 8 s. The temperature of the mass spectrometer transfer line was 290 °C and ion source 280 °C.

Data processing was conducted using GC Image™ v2.1 software (Zoex). The scan range was *m/z* 50–600.

Higher accuracy GCxGC/TOFMS analyses were undertaken using an Agilent 7890A gas chromatograph fitted with a Zoex ZX2

thermal modulator interfaced with a AccuTOF GCv time-of-flight mass spectrometer (Jeol Inc., Peabody, MA, USA) operated in positive ion EI mode. The scan speed was 25 Hz. The first-dimension column was a 100% dimethyl polysiloxane DB-1 (20 m×0.25 mm×0.25 mm; Agilent Technologies J & W, Wilmington, DE, USA) and the second dimension column was a 50% phenyl methylpolysiloxane BPX-5 (2 m×0.1 mm×0.05 mm; Agilent Technologies J & W, Wilmington, DE, USA). Helium was used as carrier gas kept at constant pressure 300 KPa. Samples (1 mL) were injected at 250 °C splitless. The oven was programmed from 40 °C (held for 5 min) and then heated to 300 °C at 2.5 °C min⁻¹ (held at 300 °C for 20 min). The modulation period was 12 s. The mass spectrometer transfer line temperature was 270 °C and the ion source temperature 250 °C. The scan range was *m/z* 40–550. Predicted values for selected physical constants of molecules were modelled with Spartan 10 software (Wavefunction Inc., Irvine, CA, USA).

RESULTS AND DISCUSSION

GCxGC/TOFMS of the methylated OSPW sample from the tailings pond revealed a number of very well-resolved peaks (Figs. 1(a)–1(d)). These compounds were also detected herein in numerous other OSPW extracts, from the same and other tailings ponds, and can thus probably be considered common constituents of at least some stored process waters.

The EI mass spectrum of component I (Fig. 2(a)) contained an apparent molecular ion at *m/z* 252, albeit at low intensity (6% of base peak ion intensity). The accurate mass of this ion was measured by GCxGC/TOFMS as 252.136, close to the theoretical monoisotopic mass of an ion with composition [C₁₄H₂₀O₄]⁺ (252.13561). A base peak was observed at *m/z* 193 (Fig. 2(a)), suggesting that the unknown might be an ester of a disubstituted adamantyl acid in which the *m/z* 193 ion can be attributed to the loss of a COOCH₃ fragment (59 Da) from the molecular ion. The second most abundant ion (*m/z* 133) in the spectrum was identified as being formed by charge retention on the adamantane core structure after the loss of two such methylated acid groups and the transfer of an H from the adamantane core to the leaving group.

The EI mass spectrum of component II showed a molecular ion *m/z* 266 of very low intensity (4%, Fig. 2(b)). This, combined with a low abundance of the compound, resulted in a poor spectral peak shape and ion statistics, and thus in a centroid that was not clearly defined, which prevented an accurate mass determination. The base peak at *m/z* 207 was attributed to a loss of a methylated acid group (59 Da, COOCH₃) from the molecular ion, the ion with the second largest intensity (*m/z* 133) was again explained by charge retention on the adamantane core after loss of both methylated acid groups and one H. The ion at *m/z* 193 was assigned to the loss of CH₂COOCH₃ (73 Da), i.e. the ethanoic acid methyl ester group.

Analysis of a mixture of methylated standards containing derivatised noradamantane carboxylic, bis-derivatised adamantane-1,3-dicarboxylic and 3-carboxymethyladamantane-1-carboxylic acids showed that the esters of the diacids eluted at identical retention times and possessed mass spectra (Figs. 2(b) and 2(d)) virtually identical to those of the two unknowns I and II (Figs. 2(a) and 2(c), *R*_{t1}=63.3min/*R*_{t2}=6.6 s vs *R*_{t1} = 63.3 min/*R*_{t2} = 6.7 s for standard and unknown, I, respectively; *R*_{t1} = 67.5 min/*R*_{t2}=6.8

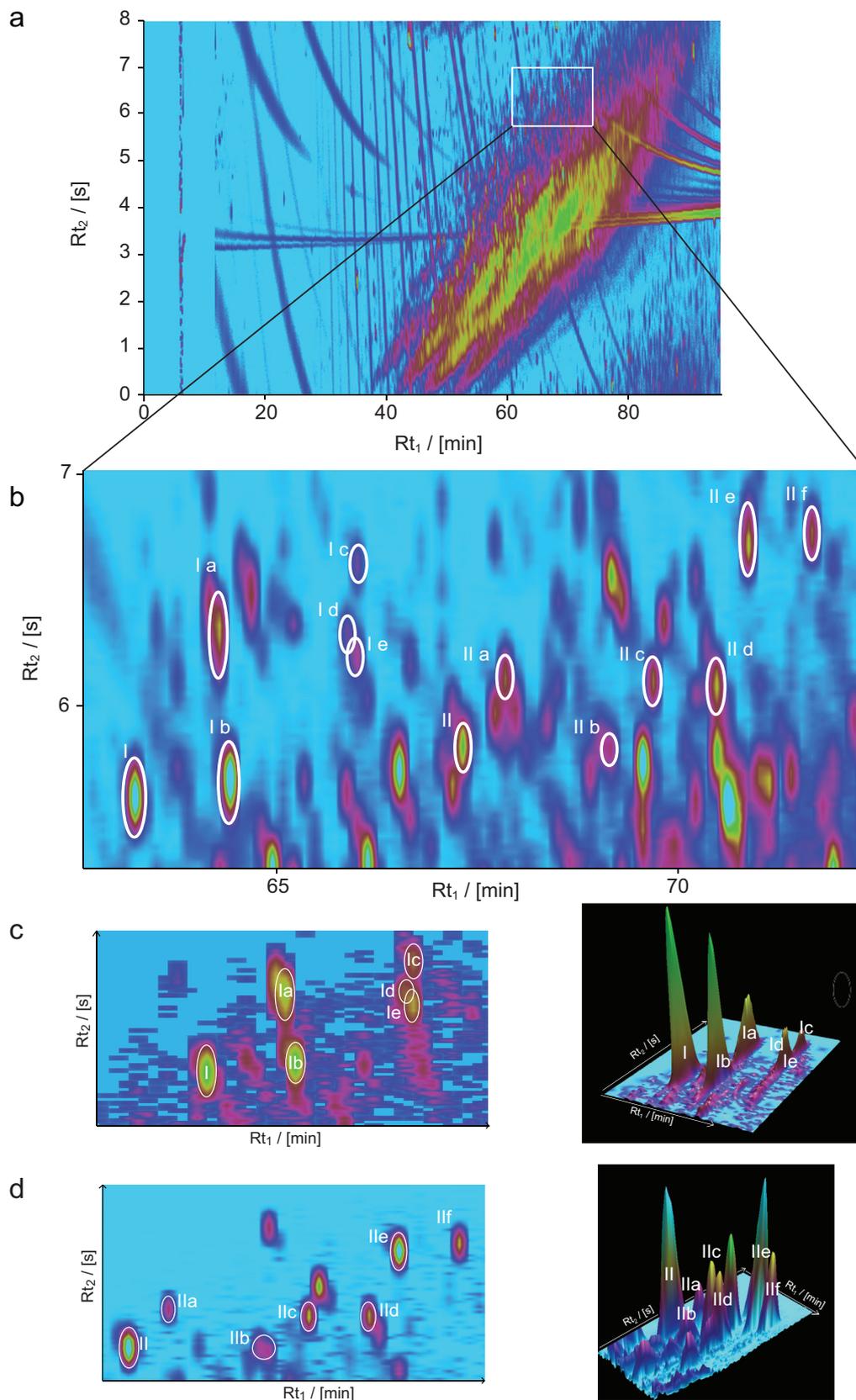


Figure 1. (a) Whole EI total ion current (TIC) chromatogram and (b) partial EI TIC chromatogram (retention time, Rt_1 61–74 min, Rt_2 5.5–6.5 s). Diacids are shown labelled with I ($[M]^+ \cdot m/z$ 252) and II ($[M]^+ \cdot m/z$ 266), where structures I and II were confirmed by comparison with spectra and Rt of authentic acids and Ia–e and IIa–f are tentatively assigned as other isomers (for which spectra are shown in Figs. 2 and 3). (c) Extracted ion current (EIC) 2D and 3D chromatogram representations for ions m/z 191.5–193.5 showing I and (d) isomers and (d) EIC 2D and 3D chromatogram representations for ions m/z 205.5–207.5 showing II and isomers.

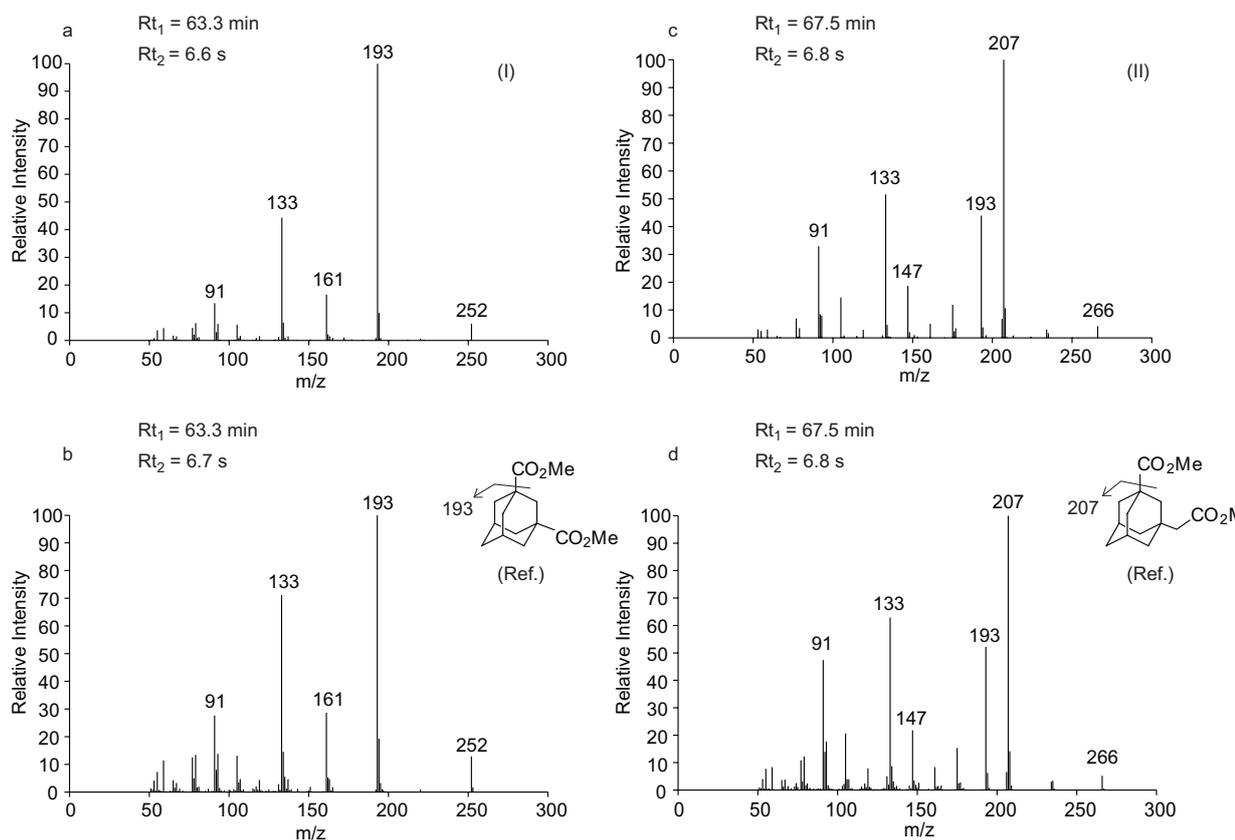


Figure 2. EI mass spectra and retention times of methyl esters of (a, c) unknown compounds (I, II) and the dimethyl esters of (b) adamantane-1,3-dicarboxylic acid and (d) 3-carboxymethyladamantane-1-carboxylic acid.

s for both standard and unknown, II). Addition of ca 50 ng of d_3 -noradamantane carboxylic acid methyl ester as a retention time reference compound, yielding an easily recognisable mass spectrum with a molecular ion at m/z 183, allowed more precise matching of GCxGC retention times between different chromatographic analyses. Using GC Image software, accurate retention time matches were found in the OSPW for both diacids (Fig. 1, I and II, and Fig. 2). Previous work has shown the presence of O_4 species in OSPW but no acid structures were identified by 1H -NMR, FTIR or FTICR/HRMS.^[11–14] In addition to these individual C_{12} and C_{13} diacids confirmed with reference compounds, other isomers of the two species could be detected and more tentatively assigned from the EI mass spectra of the esters (Fig. 3, Ia–e, IIa–f). The spectra all contained the same molecular ions as I or II (m/z 252 and 266, respectively), but differed in intensities of the other ions, including the base peaks.

Thus, peaks Ia–Ie were tentatively assigned as isomers of I due to apparent molecular ions at m/z 252. In theory, a total of eight structural and steric isomers of such a diacid are possible (excluding enantiomers), i.e. in addition to the 1,3-disubstituted adamantane the 1,2-, 2,4-isomers, two isomers of the 1,4-, 2,6-disubstituted adamantane and maybe the dimethyl adamantane-2,2-dicarboxylate (which might not be favoured for steric reasons).^[16] While Ib and Ic showed a base peak at m/z 193, indicating a loss of $COOCH_3$, the base peak of Id and Ie was at m/z 192, suggesting the loss of the methyl ester molecule via a concerted process involving H-transfer from the charge-retaining fragment, as shown by Waltman and Ling,^[17] who described such fragmentations in detail.

This has also been reported previously for the EI mass spectrum of the methyl ester of adamantane-2-carboxylic acid.^[10] The spectrum of compound Ia showed that the ions of m/z 192 and 193

had similar intensities. Favouring of a hydrogen transfer strongly suggests that at least one of the substituents is placed on a distal carbon atom, i.e. neighbouring a bridgehead, where removal of H will result in the formation of a tertiary carbocation. Another feature of these isomers is the higher intensity of m/z 220, corresponding to a loss of 32 Da (i.e. CH_3OH) from the molecular ion, also indicating that at least one of the carboxy groups is placed on a distal carbon, since with substitution on a bridgehead (or 'apical' carbon), the loss of the complete carboxy group would be favoured in order to produce a tertiary carbocation.

We can thus speculate that these spectra correspond to the 1,2-, 1,4-, 2,4-, 2,6-diacid isomers, and perhaps also the dimethyl adamantane-2,2-dicarboxylate. For diacids such as II, there are 14 possible isomers excluding enantiomers. Six peaks in the chromatogram eluting in the same region as II (Fig. 1) showed EI mass spectra that were similar to that of II. The mass spectra of the peaks IIa–IIf showed a weak molecular ion at m/z 266 (0.3–13%; Fig. 3), thus allowing tentative identification of these compounds as isomers of II.

As discussed for I, the main differences in the mass spectra were the loss of the carboxy methyl group as such or plus a hydrogen (–59 or 60 Da), resulting in the formation of fragment ions at m/z 207 or 206. In addition, the loss of CH_3OH (32 Da) resulted in the formation of a fragment ion at m/z 234 of varying intensity. All these isomers were also present in other OSPW extracts from Canadian tailings ponds that were analysed.

Interestingly, in samples of fresh OSPW supplied by Environment Canada in 2009, which were taken from the inlet pipe to the West In-Pit tailings pond, rather than from the pond itself, Rowland et al.^[6,10] could not detect any O_4 species by GCxGC/TOFMS. Re-examination of that sample by higher accuracy

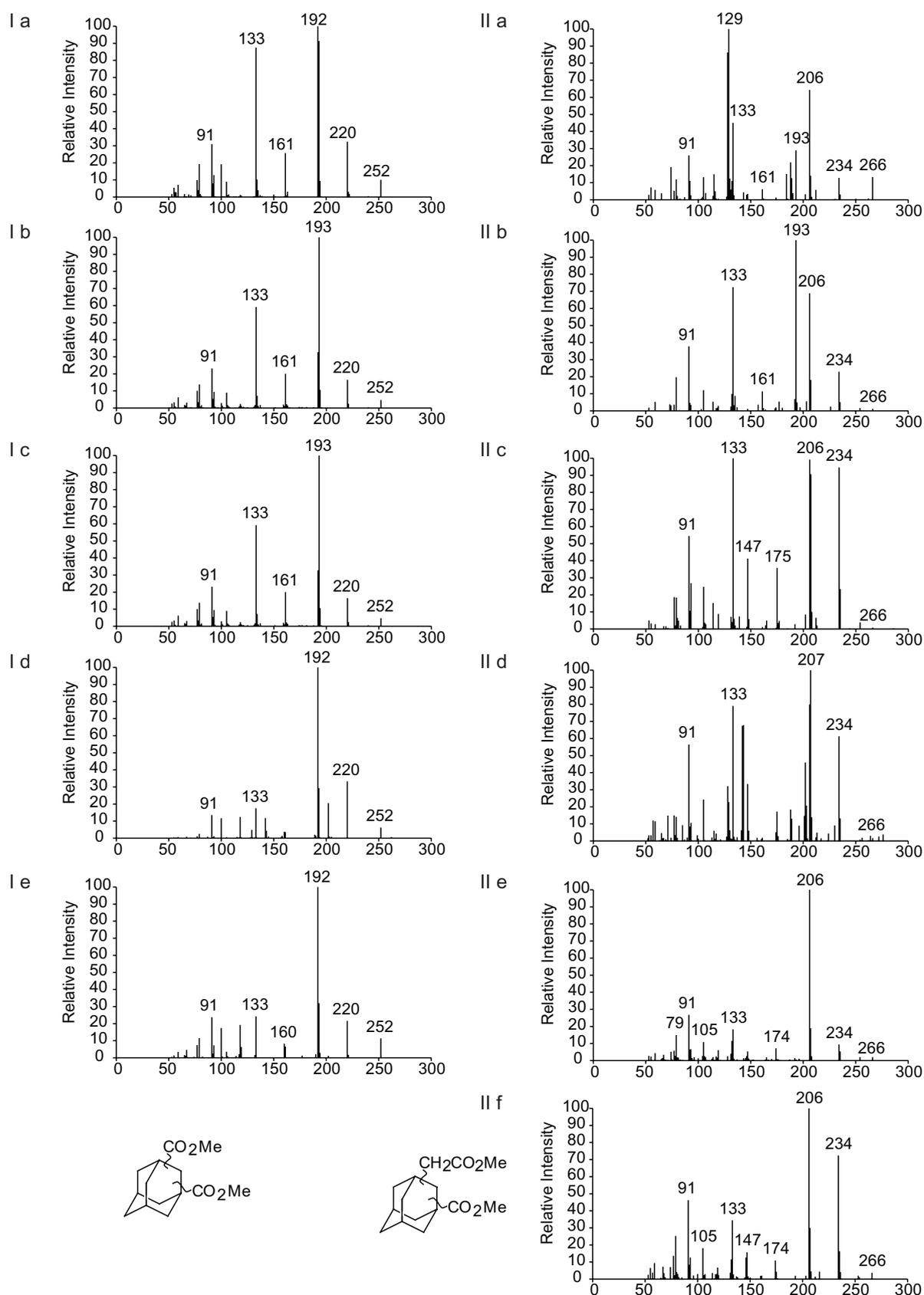


Figure 3. EI mass spectra of unknowns tentatively assigned as isomers of I and II.

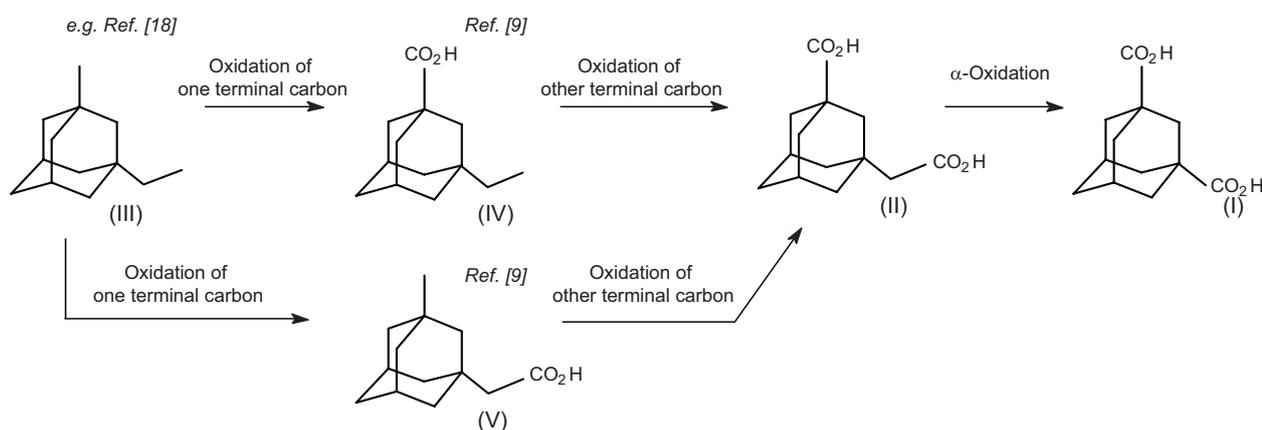


Figure 4. Speculated biodegradation pathway of alkyladamantanes. Compounds: (I) adamantane-1,3-dicarboxylic acid; (II) 3-carboxymethyladamantane-1-carboxylic acid; (III) 1-ethyl-3-methyladamantane; (IV) 3-ethyladamantane-1-carboxylic acid; (V) 2-(3-methyl-1-adamanty)acetic acid.

GCxGC/TOFMS herein confirmed that the diacids were absent. However, since the relative ratio of O_4 species to O_2 species has been shown to increase with progressing biodegradation,^[12] it is possible that the absence of diacids in the inlet pipe OSPW, and their presence in stored OSPW in the pond, reflects further in situ environmental biodegradation of the monoacids. O_2 species are presumably first generated in geological time by biodegradation of the corresponding hydrocarbons in the oil sands deposits. O_4 species, including the adamantane diacids detected here, are thus probably further degradation products of diamondoid hydrocarbons, which have been shown to be present in oil with up to five alkyl substituents of varying chain lengths.^[18] This is in line with the biological oxidation of petroleum hydrocarbons to acids and monoacids to diacids (Fig. 4). This pathway has been hypothesised previously^[19–21] to account for observed reductions in the toxicity of some OSPW with time. The proposed route entails carboxylation of a terminal carbon (Fig. 4), followed by β -oxidation of the chain if longer than two carbon atoms. An even carbon number alkyl chain attached to cyclic structures would leave a $-\text{CH}_2\text{COOH}$ substituent attached to the adamantane core, odd chains a $-\text{COOH}$. The $-\text{CH}_2\text{COOH}$ group can then be converted via α -oxidation into a $-\text{COOH}$, and potentially further degraded via β -oxidation resulting in ring opening and producing, perhaps, bicyclic or monocyclic intermediates.

The cage-like structures of the adamantanes could, however, impede ring opening and might explain why numerous diacids appear to be somewhat recalcitrant and present in several OSPW. Diacids exhibit a higher polarity than hydrocarbons or monoacids, are more water-soluble and are thus expected to show a significantly decreased log P and toxicity, as reflected, for example, in higher 50% lethal concentration values, LC_{50} .^[4] Indeed, modelling of some physical constants with Spartan software herein resulted in predicted log P values of 1.91 (I) and 1.85 (II), which are lower than the values predicted for the corresponding monocarboxylic species (2.82–4.09^[22]) or for the corresponding hydrocarbons (e.g. as high as 3.7 for the 1,3-dimethyladamantane). The increased polarity achieved by adding a second acid group to the adamantane structure shows that further biological oxidation of the hydrocarbons and monoacids to diacids would decrease toxicity, as postulated previously from modelling studies and experimentation with model diacids.^[14]

CONCLUSIONS

Two naphthenic acid ' O_4 ' compounds in OSPW from a Canadian tailings pond have been identified and confirmed by comparison with authentic compounds, using GCxGC/TOFMS. Several others have been more tentatively assigned. The presence of these diacids in an OSPW sample from a tailings pond supports previously postulated biodegradation pathways for diamondoid hydrocarbons and monocarboxylic acids. Addition of a further carboxylic acid group increases hydrophilicity and thus seems to be a natural mechanism to further decrease the toxicity of the monoacids.

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