Predicted toxicities of novel alicyclic bicyclic acids in oil sands process-affected waters

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Abstract

Alicyclic bicyclic acids have been reported to be the major naphthenic acids (NA) in oil sands process-affected water (OSPW) but due to the extreme complexity of OSPW none have yet been identified. A previous study using the Microtox™ assay indicated that some synthetic alicyclic bicyclics were the most acutely toxic acids tested so it is important that these compounds are identified and their toxicities determined.

Using comprehensive multidimensional gas chromatography-mass spectrometry (GCxGC-MS) we show that >100 C_{8-15} bicyclic acids are typically present in OSPW. Synthesis or purchase facilitated GCxGC retention times of methyl esters of these acids to be established and their mass spectra compared with unknowns. Having identified numerous alicyclic bicyclic acids by comparison with authentic standards, we suggest that many of the remaining unknowns are simply analogues of the identified acids with longer alkanoate chains and/or alkyl substituents.

Previously we reported the predicted toxicities of a range of NA, many of which had been identified in OSPW, but the alicyclic bicyclic acid structures modelled had only been found in commercial NA mixtures or crude oil. Now, having identified numerous novel acids, we report their toxicities to *Pimephales promelas* (fathead minnow), the protozoan *Tetrahymena pyriformis* and the water flea *Daphnia magna* as predicted by Admet Predictor™ (Simulations Plus). Also, neural network ensemble models were used to assess a compound's likelihood of binding to the estrogen or androgen receptors. Furthermore, the persistence of NA is a huge problem for the oil sands extraction industries so the likelihood of biodegradation was also modelled.

Predicted LC_{50}s for fathead minnows and water fleas were in the range 0.01 – 3.54 mmol/L and EC_{50}s for *T. pyriformis* 0.01 – 0.7 mmol/L. As expected for this type of structure, no binding affinities for either estrogen or androgen receptors were predicted. Of the structures tested, about 30% were considered not readily biodegradable as defined by the model based on biological oxygen demand and theoretical oxygen demand. Structures with terminal branches were least likely to readily biodegrade.

Several of the novel alicyclic bicyclic acids identified were predicted to be more toxic than the equivalent molecular weight decalin acids which were previously modelled (and experimentally tested with Microtox™) to be the most toxic of this group of compounds.

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Conclusions

- Acute effects upon *T. pyriformis* & *D. magna* predicted to be greater than for some other classes of NAs
- For fish, *P. promelas,* LC_{50}s generally predicted to be higher than for invertebrates and protozoans
- Condensed structures predicted to more toxic to *D. magna* than equivalent weight decalin acid type structures
- Predicted fish LC_{50}s similar to that measured for acute exposure to aliphatic fraction of OSPW [8]
- Many structures likely to resist biodegradation

Methods

- Bicyclic acids were either purchased from commercial suppliers or synthesised in-house. Details in Wilde *et al* (submitted to *J. Chromatogr. A*)
- Acids were identified by comparison of their mass spectra and retention times using comprehensive multidimensional gas chromatography-mass spectrometry (GCxGC-MS)
- Instrumentation and analysis was similar to West *et al* (2013)
- Toxicities and biodegradation potential were predicted using Admet™ Simulations Plus
  Models for:
  fathead minnow *Pimephales promelas*
  protozoan Tetrahymena pyriformis
  water flea *Daphnia magna*
- See Scarlett *et al* [7]

References

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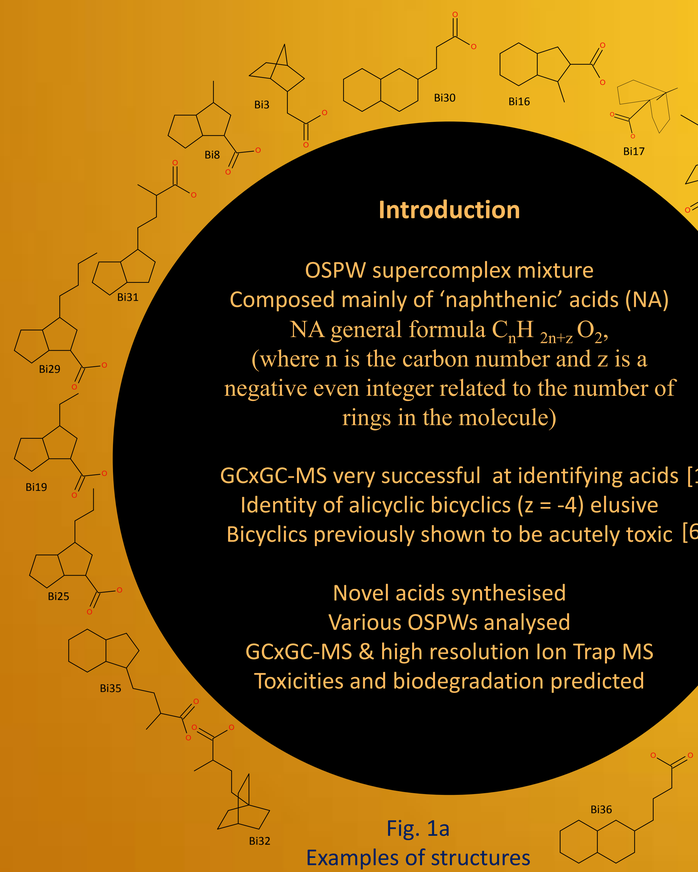
Introduction

OSPW supercomplex mixture
Composed mainly of 'naphthenic' acids (NA)
NA general formula $C_nH_{2n+z}O_2$,
(where n is the carbon number and z is a negative even integer related to the number of rings in the molecule)

GCxGC-MS very successful at identifying acids [1-5]
Identity of alicyclic bicyclics (z = -4) elusive
Bicyclics previously shown to be acutely toxic [6]

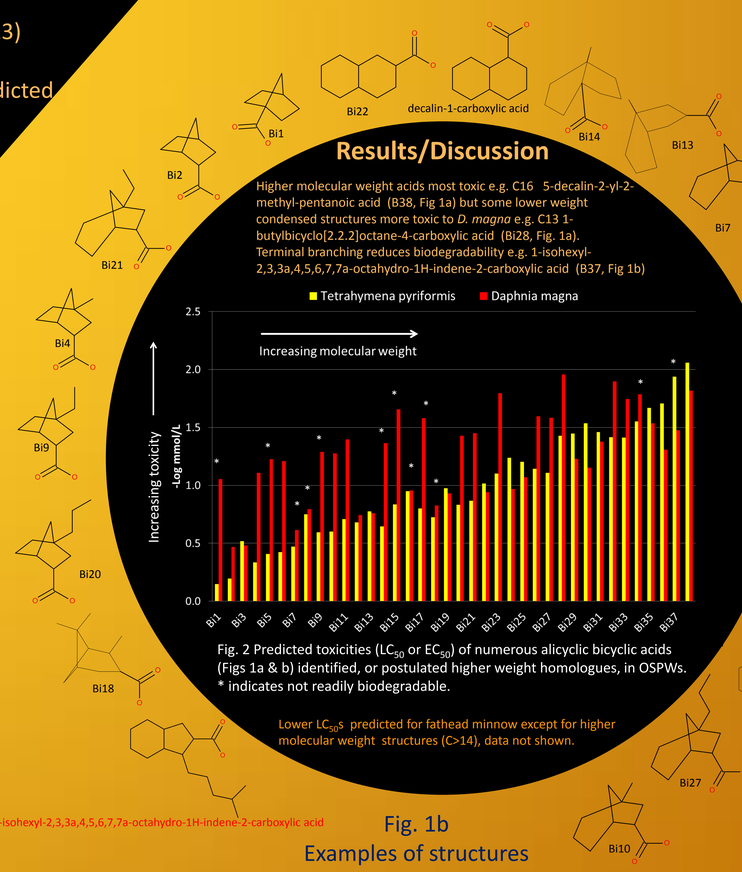
Novel acids synthesised
Various OSPWs analysed
GCxGC-MS & high resolution Ion Trap MS
Toxicities and biodegradation predicted



Bi28: 1-butylbicyclo[2.2.2]octane-4-carboxylic acid

Bi38: 5-decalin-2-yl-2-methyl-pentanoic acid

Fig. 1a
Examples of structures



Bi37: 1-isohexyl-2,3,3a,4,5,6,7,7a-octahydro-1H-indene-2-carboxylic acid

Fig. 1b
Examples of structures

Results/Discussion

Higher molecular weight acids most toxic e.g. C16 5-decalin-2-yl-2-methyl-pentanoic acid (B38, Fig 1a) but some lower weight condensed structures more toxic to *D. magna* e.g. C13 1-butylbicyclo[2.2.2]octane-4-carboxylic acid (Bi28, Fig. 1a). Terminal branching reduces biodegradability e.g. 1-isohexyl-2,3,3a,4,5,6,7,7a-octahydro-1H-indene-2-carboxylic acid (B37, Fig 1b)

Fig. 2 Predicted toxicities (LC_{50} or EC_{50}) of numerous alicyclic bicyclic acids (Figs 1a & b) identified, or postulated higher weight homologues, in OSPWs. * indicates not readily biodegradable.

Lower LC_{50}s predicted for fathead minnow except for higher molecular weight structures (C>14), data not shown.

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