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Diaromatic sulphur-containing 'naphthenic' acids in process waters

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ABSTRACT

Polar organic compounds found in industrial process waters, particularly those originating from biodegraded petroleum residues, include 'naphthenic acids' (NA). Some NA have been shown to have acute toxicity to fish and also to produce sub-lethal effects. Whilst some of these toxic effects are produced by identifiable carboxylic acids, acids such as sulphur-containing acids, which have been detected, but not yet identified, may produce others. Therefore, in the present study, the sulphur-containing acids in oil sands process water were studied.

A fraction (*ca* 12% by weight of the total NA containing *ca* 1.5% weight sulphur) was obtained by elution of methylated NA through an argentation solid phase extraction column with diethyl ether. This was examined by multidimensional comprehensive gas chromatography-mass spectrometry (GCxGC-MS) in both nominal and high resolution mass accuracy modes and by GCxGC-sulphur chemiluminescence detection (GCxGC-SCD).

Interpretation of the mass spectra and retention behaviour of methyl esters of several synthesised sulphur acids and the unknowns allowed delimitation of the structures, but not complete identification. Diaromatic sulphur-containing alkanoic acids were suggested.

Computer modelling of the toxicities of some of the possible acids suggested they would have similar toxicities to one another and to dehydroabietic acid. However, the sulphur-rich fraction was not toxic or estrogenic to trout hepatocytes, suggesting the concentrations of sulphur acids in this sample were too low to produce any such effects *in vitro*. Further samples should probably be examined for these compounds.

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1. Introduction

Naphthenic acids (NA) are reported to be amongst the toxic polar constituents of produced water from various petroleum production processes, including from conventional and from less conventional petroleum reserves, such as oil sands. Deposits of oil sands have been found as far apart globally as China, Venezuela and Canada and are a major source of fossil fuels (e.g. Bycott et al., 1999; Gosselin et al., 2010). The oil sands of Alberta, Canada exceed most conventional oil reserves in volume. These remained uneconomic for many years due to the costs of removing the oil from the sand, but are now produced from both surficial and sub-surface deposits (Gosselin et al., 2010). Surficial deposits are processed by the Clark process in which treatment with an aqueous solution of hot alkali removes sand, fines and unwanted organic acidic material from the bitumen. A by-product of the process, after much recycling of the alkaline water, is a large volume of process-affected water (OSPW), containing sediment and organic compounds, which is currently stored in lagoons (Gosselin et al., 2010). There are concerns about possible leakage of OSPW into the surrounding environment (Kean, 2009; Schindler, 2010; Jordaan, 2012). The water is alkaline, saline and typically contains up to about 100 mg L^{-1} of a complex mixture of organic compounds including the thousands of carboxylic acids known as NA. The latter term has become used because the infrared spectrum of the acidic extract resembles that of NA refined from petroleum (MacKinnon and Boerger, 1986). However, increasingly detailed chemical and biological analyses of the OSPW NA mixtures have indicated that there are many other compounds in OSPW than in commercial refined NA and that some of the NA differ in structure (Rowland et al., 2011a), proportions (Grewer et al., 2010), biodegradability and toxicity (Scott et al., 2005) from the NA in commercial refined samples. This may be due to the refining and production methods used to obtain the latter. It is possible that the NA in oil sands are more similar to those in biodegraded unrefined petroleum (e.g. Watson et al., 2002), but few detailed analyses of the latter have been made to date.

Several toxicological effects have been attributed to NA (reviewed by Scarlett et al., 2012). For instance, when an acid extract of a whole OSPW was fractionated by distillation of the NA fraction esterifiable with diazomethane (Frank et al., 2008) the acute toxicity to bacteria in a screening assay was EC_{50} ~ 40–60 mg L^{-1}.

Furthermore, when OSPW NA were fractionated by argentation solid phase extraction (Ag^+ SPE), a fraction eluting with 5% diethyl ether: 95% hexane and containing aromatic acids, was at least as toxic as the alicyclic NA (Scarlett et al., 2012). It was also apparent from the latter fish assay that some of the toxicity of the esterifiable NA was not accounted for by the alicyclic and aromatic acids alone (Scarlett et al., 2012).

Fractions of the NA from Ag^+ SPE, including diethyl ether and methanol eluates, have not yet been fully characterised or assayed for toxicity. The diethyl ether fraction, which is the subject of the present report, contained aromatic compounds, as shown by C/H ratios and UV spectrophotometry, but in addition, about 50% of the total sulphur associated with the NA was present in this fraction (Jones et al., 2013). Multidimensional comprehensive gas chromatography (GCxGC) with sulphur chemiluminescence detection (SCD) established that several major GC-resolvable sulphur compounds were present (Jones et al., 2013).

Numerous analyses of other OSPW acid extracts by electrospray ionisation Fourier Transform Ion Cyclotron Resonance Mass Spectrometry (FT-ICR-MS) or Orbitrap MS have also indicated that a variety of sulphur species are often present (e.g. Barrow et al., 2010; Bataineh et al., 2006; Headley et al., 2011a,b). More attention has been drawn to these sulphur compounds as more has begun to be understood about the NA in OSPW, and indeed in petroleum generally (e.g. Headley et al., 2011a,b; Panda et al., 2009).

In the present study a sulphur-containing diethyl ether eluate Ag^+ SPE fraction of a methylated (esterifiable) OSPW extract was examined by GCxGC-MS with both nominal and high resolution (HR) mass accuracy modes and by GCxGC-SCD/flame ionisation detection (FID). Several acids were synthesised for comparison. The toxicity of the fraction was determined as cytotoxicity and estrogenicity in a rainbow trout *in vitro* (hepatocyte) assay and acute toxicity (lethality) for Fathead minnow (***Pimephales promelas***) **and** the water flea (*Daphnia magna*) predicted.

2. Materials and methods

Authentic acids were purchased from Sigma (Poole, U.K.) or synthesised. Syntheses were based on Friedel–Crafts acylation or alkylation of either dibenzothiophene (Sigma, Poole, UK) or naphtho[2,1-*b*]thiophene synthesised previously (Kropp et al., 1997), with methylsuccinic anhydride or β-butyrolactone (Sigma, Poole, U.K.) in the presence of aluminium trichloride (Fig. 1). The methods were essentially those of Smith et al. (2008). The resulting keto acids (from acylation) were reduced to the acids by Huang-Minlon modification of the Wolff–Kishner reaction (cf Smith et al., 2008).

The fractionated OSPW extract was obtained from Syncrude West In-Pit as described previously (Reinardy et al., 2013; Scarlett et al., 2012). Smaller amounts of an acidic extract from a different oil sands company (wishing to remain anonymous) was also obtained at a different time and location in order to briefly test the generality of occurrence of the sulphur compounds in OSPW-derived NA (Rowland et al., 2012).

Both authentic acids and OSPW NA extracts or fractions were converted to the methyl or trideuteriomethyl esters as stated previously (West et al., 2013). Argentation SPE was conducted essentially as previously (Jones et al., 2012).

Multidimensional comprehensive gas chromatography-mass spectrometry (GCxGC-MS) and GCxGC-SCD/FID analyses were conducted on four different instruments; two allowed GCxGC-MS with nominal mass resolution, one with higher mass resolution. One of the nominal mass instruments used an identical configuration of GC columns to that installed in a GCxGC-SCD/FID instrument to allow ease of comparison between the SCD/FID responses and the mass spectrometer. Details are provided in the online supplementary information (Table 1S).