Application of GC×GC-ToF-MS for identification of alkylated naphthalenes within tissues of oil-contaminated wild mussels and comparison with laboratory oil-exposed mussels

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Introduction

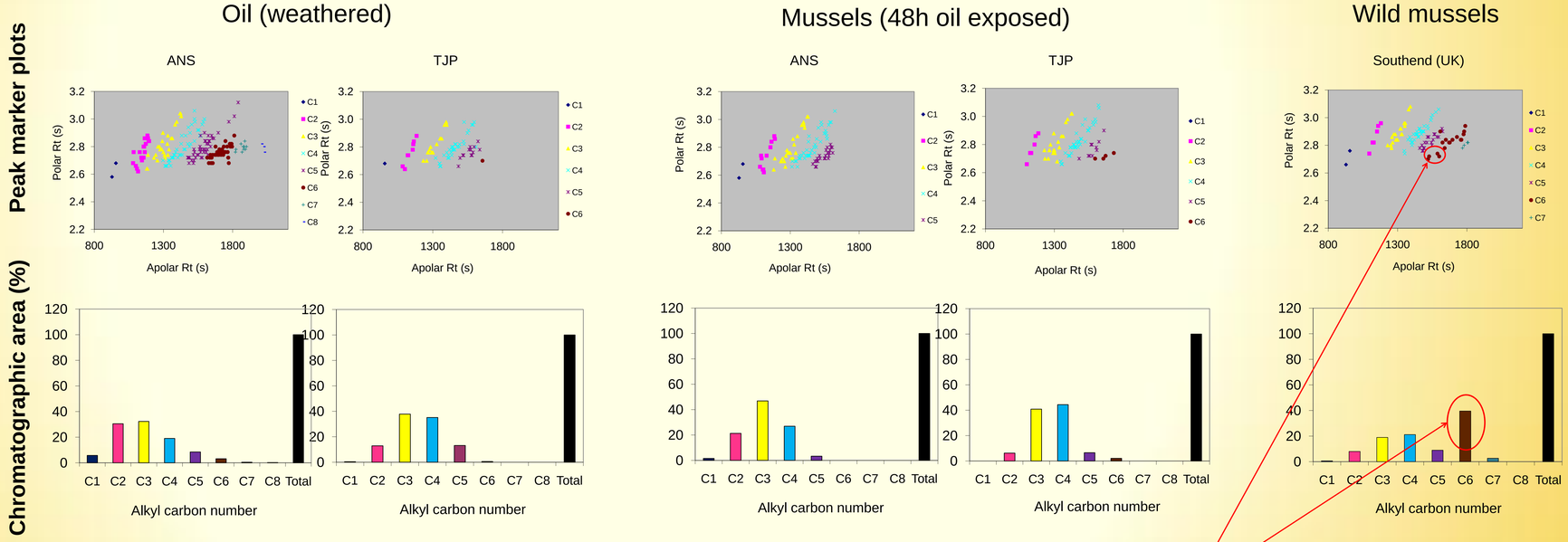
Alkylated naphthalenes are major constituents of water soluble fractions of crude oils, dominate oil industry produced waters and are common contaminants within tissues of marine biota, such as the mussel, *Mytilus* spp. It is important that environmental monitoring studies do not ignore these toxic compounds. However, most studies only rarely report alkyl naphthalenes with alkyl substituents >C_3, possibly due to the complexity involved with the separation of the thousands of isomers which are theoretically possible. In this study we use GCxGC-TOF-MS to compare alkylnaphthalenes accumulated in lab-exposed and wild mussels.

Method

Mussel collection and tissue extraction Wild mussels were collected and tissues extracted as described by Booth *et al* (2007). Collection of mussels for laboratory tests, exposure conditions, tissue extractions and analyses were as described by Frenzel *et al* (2010, In Press). In brief, mussels were subject to 48h semi-static exposure to aromatic fractions of Alaskan North Slope (ANS) and Tia Juana Pesado (TJP) crude oils. The tissues were extracted in methanol by alkaline saponification, solvent exchanged into hexane followed by alumina column clean-up.

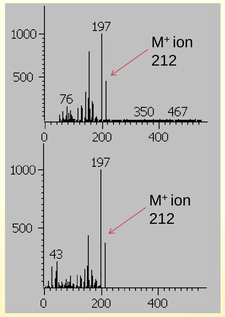
Comprehensive GCxGC-ToF-MS. Tissue extracts were analysed on a Pegasus 4D GCxGC-ToF-MS system, based on a Agilent 6890 gas chromatograph interfaced to a Pegasus III time-of-flight mass spectrometer (LECO, St.Joseph, MI). The system used the following parameters: injector 300 °C; transfer line 280 °C. The first-dimension column was a 5% phenyl-95% methyl-polysiloxane 10m × 0.18mm × 0.25μm HP-5), and the second-dimension column was a 14% cyanopropylphenyl-polysiloxane 1m× 0.1 mm × 0.1μm BP-10). Conditions were as described by Booth *et al* (2007).

Results



Typical mass spectrum for isolated C_6 group →

NIST library match 2,6-diisopropylnaphthalene →



Distinct group of diisopropylnaphthalenes (DIPN) prominent in wild mussels compared with lab exposed mussels and both crude oils

↓

Possible sources include waste paper processing, recycled paper packaging and use as plant growth inhibitor (2,6-DIPN only)

Conclusions

- **Good agreement between laboratory- and field-exposed mussel accumulation patterns**
- **Groups C_3 and C_4 alkyl chain naphthalenes dominating in terms of the number of resolved peaks and chromatographic area.**
- **GCxGC-ToF-MS was able to resolve and produce useful mass spectra of naphthalenes with up to C_7 alkyl substituents.**
- **Interference from other compounds prevented clear resolution of >C_7 compounds.**
- **Group of C_6 alkylated naphthalenes (molecular weight 212) within the tissues of Southend mussels inconsistent with origins from crude or refined oils**
- **Hypothesise C_6 isomers originate from paper industry wastes**

References

- Booth, A.M., Sutton, P.A., Lewis, C.A., Lewis, A.C., Scarlett, A., Chau, W., Widdows, J., Rowland, S.J., (2007) Unresolved Complex Mixtures of Aromatic Hydrocarbons: Thousands of Overlooked Persistent, Bioaccumulative, and Toxic Contaminants in Mussels. *Environ. Sci. Technol.*, 41(2), 457-464.
- Frenzel, M., Scarlett, A., Rowland, S.J., *et al* (2010, In Press) Complications with remediation strategies involving the biodegradation and detoxification of recalcitrant contaminant aromatic hydrocarbons *Sci. Total. Environ*.

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