Integrated assessment of oil pollution using biological monitoring and chemical fingerprinting

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Key research questions

• How do pollutants damage living systems?
• What makes some organisms more vulnerable than others?
• Can we predict the consequences for individuals, populations and communities?
UK Hydrographic office shipwrecks database
Measuring pollution
Risk assessment

• Value judgements about pollution require a quantitative assessment of the significance of the biological and ecological impact of inputs to the environment
Ecological Risk Assessment

- Hazard identification
- Exposure assessment
- Dose response assessment
- Risk characterisation
- Risk management

Accept risk
More data
Reject risk

• Chemical analysis: water, sediment, tissues
• Biomarkers: sublethal toxicity
• Bioassays: survival, growth, reproduction,
• Ecological surveys
Ecological Risk Assessment

- Hazard identification
- Exposure assessment
- Dose response assessment
- Risk characterisation
- Risk management

- Chemical analysis: water, sediment, tissues
- Biomarkers: sublethal toxicity
- Bioassays: survival, growth, reproduction
- Ecological surveys

Accept risk, More data, Reject risk
Crude oil

- Carbon: 83-87%
- Hydrogen: 10-14%
- Nitrogen: 0.1-2%
- Oxygen: 0.1-1.5%
- Sulfur: 0.5-6%
- Metals: <1000 ppm

Complex mixture of hydrocarbons of C4>26, straight chains, branched chains, cyclics, aromatics, polyaromatics…..
Oil components

- **Alkanes (paraffins) \( C_nH_{2n+2} \)**
  - \( n<5 \), gas
  - \( n=5-8 \), gasoline (petrol)
  - \( n=9-16 \), diesel fuel and kerosene
  - \( n=>10 \), fuel oil, lubricating oil

- **Cycloalkanes, \( C_nH_{2n} \)**
  - as above but higher bpt

- **Aromatic hydrocarbons \( C_nH_n \)**
  - Incomplete combustion possible
Gas chromatography mass spectrometry (GC-MS) trace of crude oil

C2-6

Larger, branched, more hydrophobic, C10+

Increasing size
Oils vary in character

Shetland: heavy, waxy

North sea: light, sulphurous
Gas chromatography mass spectrometry (GC-MS) trace of crude oil

- Low mol wt, volatile compounds evaporate or are bio-degraded first.
- Larger, branched hydrophobic compounds can bind sediments and bio-accumulate.
‘weathered’ oils

(UCM = unresolved complex mixture)
Toxicity
Toxicity

Benzo(a)pyrene → B(a)P epoxide

Unresolved complex mixtures → Radical cations → DNA adducts, oxidative damage, immunotoxic, genotoxic, narcotic effects
Adverse outcome pathway

--- subcellular --- cellular --- individual --- population

Modes of action

Reactive oxygen species

Transcription factor activation

Oxidative damage

Inflammation

Disease susceptibility

Developmental abnormalities

Increased metabolic demand

Reduced growth

Reduced offspring viability

Damage to major organs

Population decline

DNA adduct formation

Elevated antioxidant responses

Stress response

Apoptosis

Mutations

Altered P450 gene expression

Necrosis

Mutations
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ENVIRONMENTALLY HAZARDOUS SUBSTANCES

Liquids
Bisphenol A-epichlorohydrin-epoxy resin 2400 Kg
Tris(1,3-dichloroisopropyl) 3600 Kg
Isophoronediamine nonylphenol 30 Kg
Glyphosate 16640 Kg
Dibutyltin diacetate 50Kg
Dibutyltinoxide 412 Kg
Propaquizafop 13816 Kg
Profenofos 5728 Kg
Carbendazim 1200 Kg
Alkylphenol 7088 Kg
Hexamethylindanopyran 844 Kg

Organometalic compounds, caustic alkali liquid, acid (sulphuric), organic solvents, etc…
Contamination screening survey

30-31 January 2007

SAMPLING STATIONS
Chemical analysis

Synchronous scan, SIM acquisition GC-MS: high accuracy and precision at trace levels
Biomarkers

- Lysosomal Stability
- Immune Function
- Oxidative Stress
- DNA damage
- Cholinesterase activity.
Lysosomal stability
DNA damage
Immune function
Results (Aliphatics)

Napoli; IFO-380 heavy oil

Surface microlayer lubricating oil; diesel

Limpet shells

Nothing detected
PAH distribution in Lyme Bay

Surface microlayer Total PAH Concentrations (ng/L)

Subsurface water Total PAH Concentrations (ng/L)
Origin (pyrolytic/petrogenic)

Surface microlayer Fl/Py Ratio

Subsurface water Fl/Py Ratio
Biomarkers post second spill
Aliphatic fraction profile m/z = 85

Napoli oil

limpets

sea water
Terpanes
m/z = 191

Napoli oil

limpets

sea water
Tissue residue analysis

Chesil beach
Branscombe
pre-spill
Branscombe
post-spill A
Branscombe
post-spill B
Branscombe
post-spill C
Chrysene
Pyrene
C3 phenanthrenes
C2 phenanthrenes
C1 phenanthrenes
Phenanthrene

Tissue concentration (µg/g dry weight)

0 1 2 3 4 5

Chesil beach
Branscombe
pre-spill
Branscombe
post-spill A
Branscombe
post-spill B
Branscombe
post-spill C
Chrysene
Pyrene
C3 phenanthrenes
C2 phenanthrenes
C1 phenanthrenes
Phenanthrene
Conclusions

• Oil on limpets July 2007 IS from Napoli salvage
• Combining biomarkers and chemical fingerprinting allows study of causal relationships
• ……Long term ecological effects?
Adverse outcome pathway

- subcellular
- cellular
- individual
- population

Exposure/Passive samplers?
- Ingestion
- Damage to membranes
- Oxidative damage
- DNA adduct formation
- Altered P450 gene expression
- Transcription factor activation

Bioassays/Toxkits?
- Disease susceptibility
- Developmental abnormalities
- Reduced growth
- Population decline
- Increased metabolic demand
- Reduced offspring viability
- Damage to major organs
- Stress response
- Apoptosis
- Necrosis
- mutations

Conceptual models?
- Toxicokinetic toxicodynamic models
- Dynamic energy budget models
Acknowledgements

- Steve Rowland
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- Carlos Guitart
- James Readman

Lewis et al 2010 Environmental Toxicology and Chemistry 29:1358
Guitart et al 2009 Environmental Science and Technology 42:2275