



FINGERPRINTING OIL RESIDUES FROM AROUND ORKNEY AND SHETLAND

ERT (Scotland) Ltd has analysed oil residues collected from the coastlines around Orkney and Shetland since March 1994. The objective of the analysis is to establish the type of oil present and, if possible, to identify its source. This work has been sponsored by the Atlantic Frontier Environmental Network (AFEN) since 1996. Samples of beached oil residues, eg tarballs or oiled seabirds are currently collected by Royal Society for the Protection of Birds (RSPB) volunteers co-ordinated by Erik Meek (Orkney) and Martin Heubeck (Shetland).

THE CHALLENGE

The oil residues that are washed up on the shorelines of Orkney and Shetland are usually in the form of tarballs or attached to dead birds. Often these oil residues are badly weathered, and therefore have lost a large fraction of their original composition.

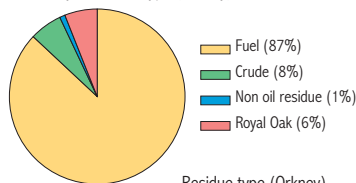
THE TECHNOLOGIES USED

Each sample received was prepared for instrumental analysis. An initial analysis was then carried out, using gas chromatography with a flame ionisation detector (GC-FID) in order to obtain a chromatographic profile of the total hydrocarbon material present in the sample. The main groups of components identified using GC-FID are the normal alkanes, the branched alkanes and the unresolved components.

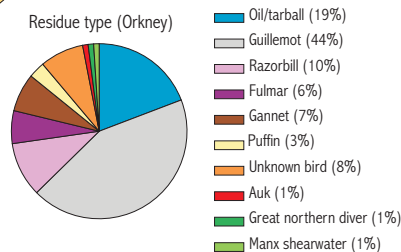
are therefore more volatile. Following further weathering of the resolved material present, a hump of unresolved material, commonly referred to as the "unresolved complex mixture" or UCM, remains. The ratio between any UCM present and the resolved components (n-alkanes) is another indicator of the degree of weathering of a particular oil. And finally, the shape of the UCM and carbon number range over which it occurs can also assist in the identification of the type of oil present.

A more detailed analysis of each oil residue is then undertaken using gas chromatography-mass spectrometry (GC-MS) to study the UCM fraction of the sample in more detail. The UCM is composed of a complex mixture of hydrocarbons, including cycloalkane compounds which will remain unchanged even after substantial weathering and biodegradation of petroleum. Using a GC-MS technique called mass fragmentography, partial resolution of the UCM is possible, enabling identification of some of these biological precursor compounds of oil; pentacyclic triterpanes and regular and rearranged steranes. These relative distribution of these so-called in an oil residue biomarker compounds – the oil's fingerprint – can be used for the purposes of source correlation.

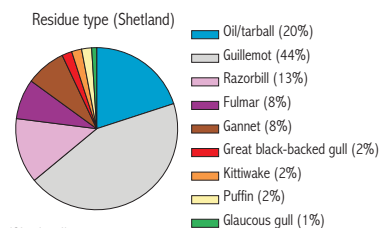
Identified Hydrocarbon type (Orkney)



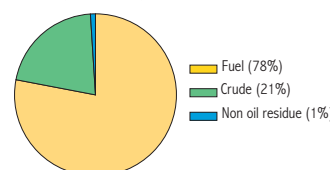
Residue type (Orkney)



Residue type (Shetland)



Identified Hydrocarbon type (Shetland)



Petroleum contains a homologous series of n-alkanes which when analysed using GC-FID can provide a chromatogram with qualitative information on the range and distribution of these components. In an unweathered state, GC analysis can be used to determine whether the oil is of petroleum origin and the type of oil eg crude oil, condensate, or whether it may be a refined product such as fuel oil, lube oil etc. Once petroleum becomes weathered, from physical and/or biological processes in the marine environment, the range and distribution of the alkanes present in the original material is significantly altered. Evidence of the degree of weathering can be ascertained from the relative losses of "front end" material in the chromatogram ie components with a lower molecular weight, which

Selected polynuclear aromatic hydrocarbons (PAH) were also studied by GC-MS.

These specific PAH are not found in crude oils but are a typical result from cracking processes used to adjust the viscosity of bunker oils.