# Tar on Your Swimming Cozzie?

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## Summary

In 1998 an investigation of the distribution and chemistry of tar balls found on beaches around the South-West peninsula of the UK was undertaken as part of a M.Sc. research project. This initiated a longer term baseline study and over the subsequent 11 years a number of final-year B.Sc. research projects, six of which are included herein, have been completed. Beaches on the north and south coasts of Cornwall and Devon have been surveyed a number of times, often during both the summer (July-September) and the winter (December-February) seasons and many have been surveyed on a number of occasions during the period (1998-2008).

Although the amount of tar may be classed as "negligible" (<1.0 g $m^{-1}$) it can originate from sources that are geographically remote from the UK. This is demonstrated by tar balls showing a biological marker signature similar to that of oil from the *Prestige*, which sank off Spain (42°15´N, 12°08´W) in November 2002.

## Introduction

The English Channel is one of the busiest waterways in the world and a significant proportion of the UK and Europe's shipping must pass close by the South-West peninsula. For example, in 2006 Milford Haven and Southampton accounted for over 25% of the UK's oil and gas traffic[1] (Department for Transport, 2006). Additionally, between 1971 and 2003 the number of visitors to Cornwall has increased from 2.9 to over 5 million[2] (Cornwall County Council, 2006) and the "beach holiday" is an important component of this phenomenon; there is the expectation that the beaches will be clean and also free of anthropogenic pollutants, including tar.

Although legislation has significantly reduced the anthropogenic input of petroleum products into the marine environment, tar ball pollution remains a serious issue in many parts of the world. A study of the tar balls found on beaches of the South-West peninsula, would provide baseline data for the region and may provide information on their source as well as spatial and temporal distributions.

## Methods

Precise methods have varied slightly over the period of study. Typically, collection of tar balls from beaches (Fig. 1) followed UNESCO guidelines[3]. In the laboratory, soluble material was isolated from individual tar balls by dissolution in dichloromethane, which was then separated by micro-column chromatography on silica into aliphatic and aromatic fractions. The fractions were subjected to GC and GC-MS using conditions commonly encountered when analysing petroleum biomarkers and hydrocarbon mixtures.

## Results

- The number and size of tar balls on the beaches studied are both spatially and temporally inhomogeneous; however, the mean loading of tar is considerably less than 1.0 g $m^{-1}$ and therefore may be termed "negligible"[4].
- The detection limit for finding tar balls may be as low as 0.001 g and, although a number of tar balls have weighed over 100 g and the largest tar ball found was almost 160 g, the majority fall in the range 0.1-1.5 g (Fig. 2; red highlighting). Interestingly, more recent data have begun to indicate tar balls weighing 2.0-2.5 g are relatively abundant (Fig. 2; orange highlighting).
- Tar accumulation on both the north and south coasts appears to correlate with wind speeds of less than *ca* 4.5 $ms^{-1}$ (~10 mph) from a south-westerly direction and wave heights of less than *ca* 1.5 m.
- Some tar balls show a full suite of *n*-alkanes and isoprenoids, reminiscent of relatively fresh oil, others have a distribution clearly indicating biodegradation has occurred.
- The distribution of *n*-alkanes and isoprenoids in the outer and inner portions of tar balls appears to be different, which presumably reflects protection of the latter from biodegradation.
- Alkyl naphthalenes and phenanthrenes are absent from the outer layer of tar balls but present inside, presumably reflecting their dissolution from the outer surface.
- Some heavily weathered tar balls show biological marker distributions similar to those found in Nigerian crude oils.
- Tar balls collected in August 2003, January 2004 and December 2004 from two beaches in Cornwall (Portreath and Praa Sands) show distinct similarities to the oil carried by the tanker *Prestige*, which sank 130 nautical miles off the Spanish coast on 19th November 2002 (Fig. 3).

## References

[1] Department for Transport (2006) *Transport Statistics Report: Maritime Statistics 2006.*
[2] Cornwall County Council (2006) *Management of Beaches and Coastal Areas in Cornwall – A Guide to Current Best Practice*. Available at http://www.cornwall.gov.uk.
[3] UNESCO (1984) *Manual for Monitoring Oil and Dissolved/Dispersed Petroleum Hydrocarbons in Marine Waters and on Beaches*. Manuals and Guides No. 13.
[4] Corbin, C.J., Singh, J.G. and Ibiebele, D.D. (1993) Tar ball survey of six eastern Caribbean Countries. *Marine Pollution Bulletin* **26**, 482-486.

## Acknowledgements

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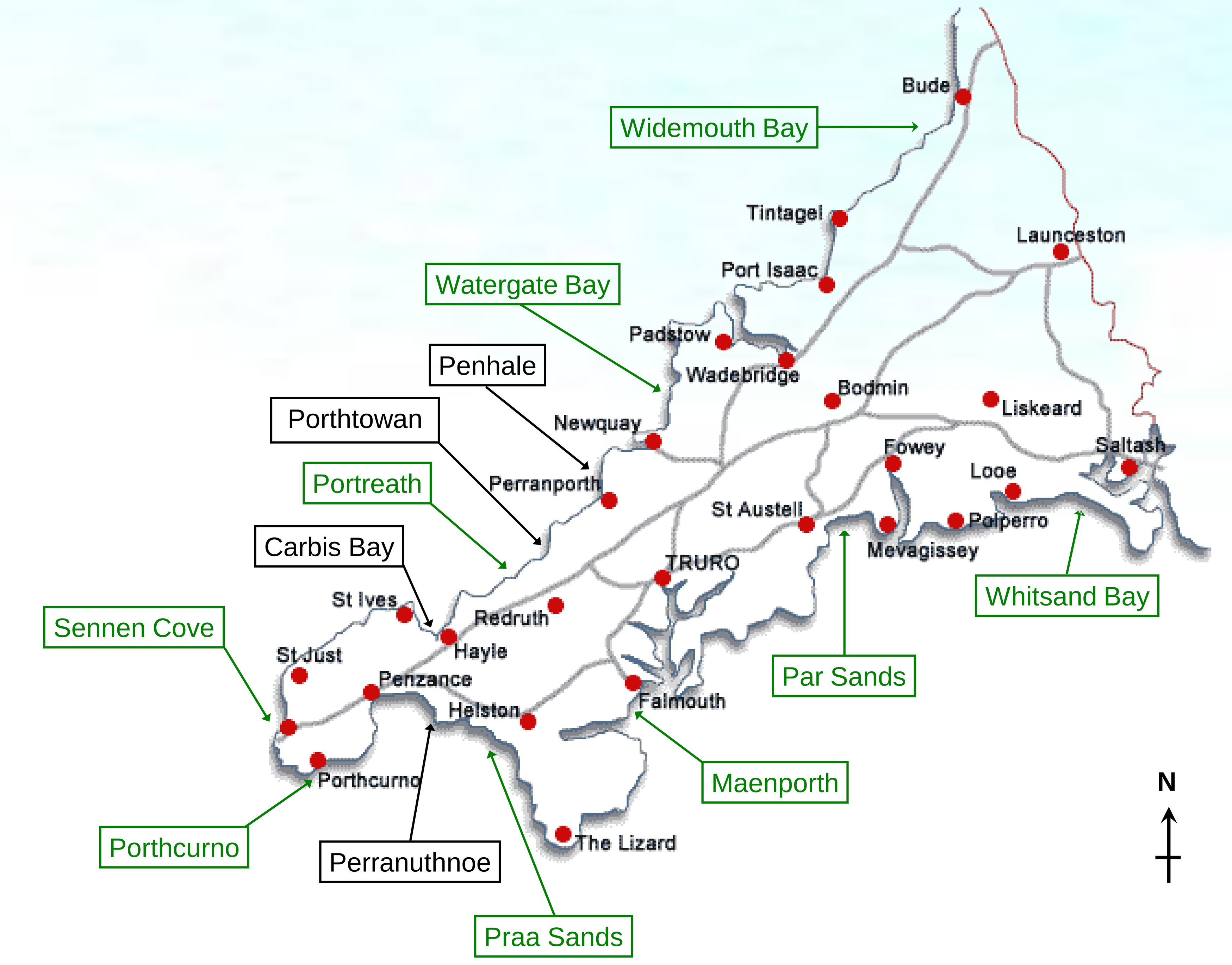


**Figure 1:** Part of the South-West peninsula of the U.K. showing the Cornish beaches studied during the period 1998-2008. Those highlighted in green have been sampled on at least two occasions.

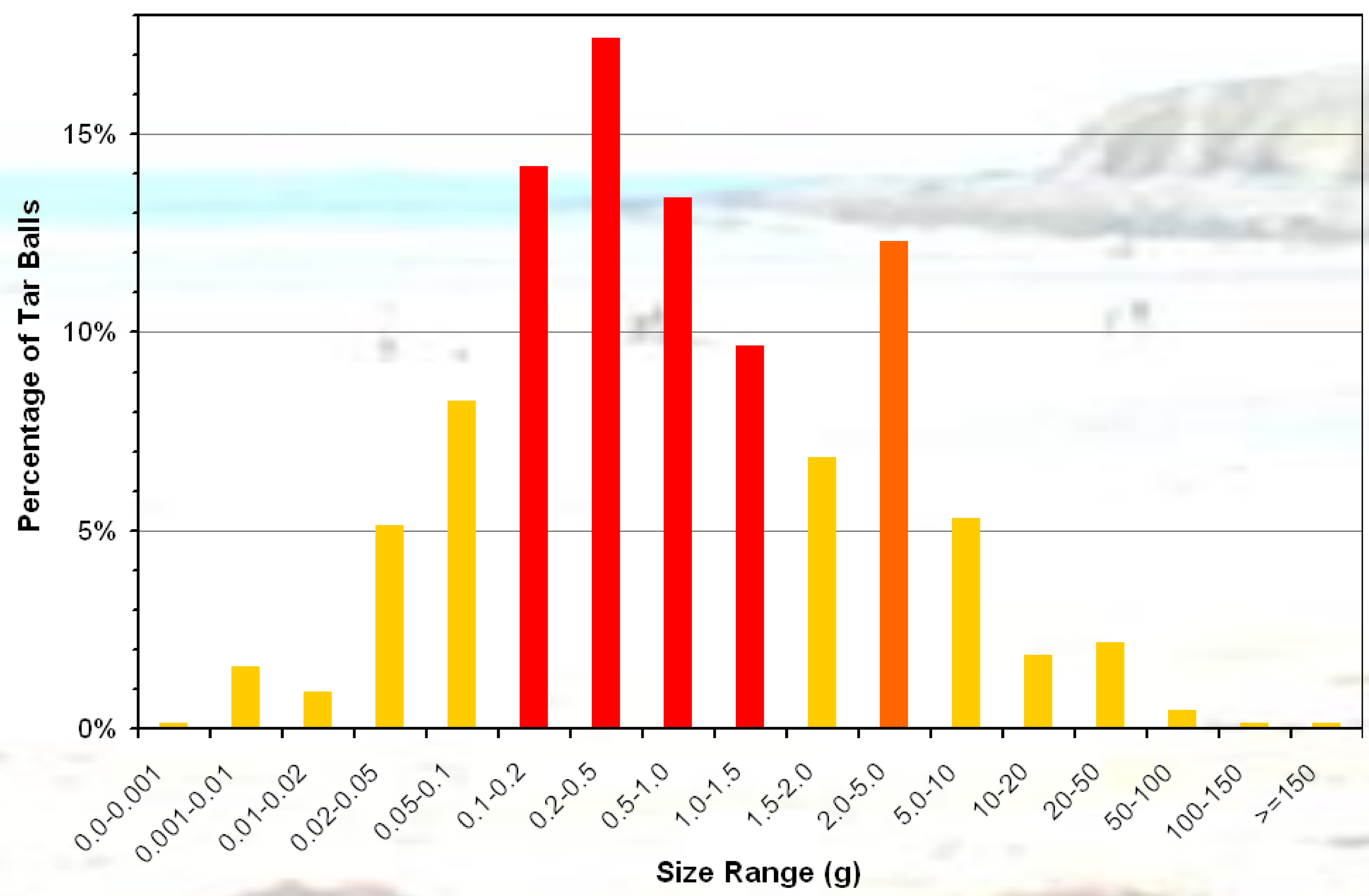


**Figure 2:** Size distribution of tar balls found on beaches of the South-West peninsula of the U.K. during the period 1998-2008

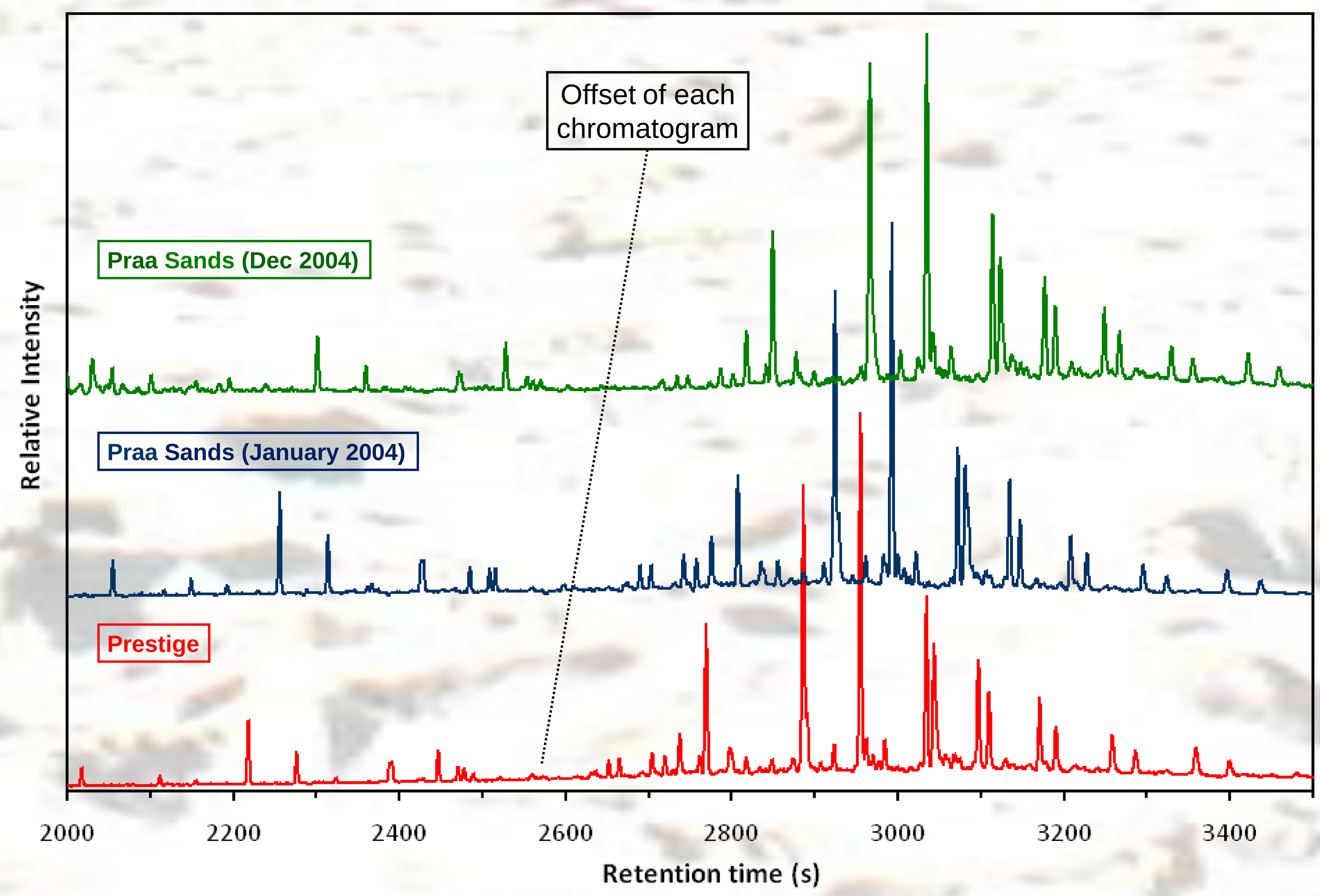


**Figure 3**: Mass chromatograms (*m/z* 191) showing the similarity of the distribution of tricyclic and pentacyclic terpanes for tar balls recovered from Praa Sands in January and December 2004 with that found in oil from the tanker *Prestige*, which sank off the Spanish coast in November 2002.