Institution: Plymouth University

Unit of Assessment: Earth Systems and Environmental Sciences B7

Title of case study: Identification and measurement of complex mixtures of organic chemicals and chemical pollutants

1. Summary of the impact (indicative maximum 100 words)

Plymouth University was the first to develop methods for identifying supercomplex 'unresolved complex mixtures' of organic chemicals, including naphthenic acids. The chemicals are of particular environmental concern (e.g. in Canada because of their production during exploitation of the oil sands and globally as they result from spillages of petroleum such as in the Deepwater Horizon spill). The methods are now used by government agencies such as Environment Canada to monitor naphthenic acid pollutants. A consortium of international oil industries (e.g., BP, Chevron, Total) also now use Rowland's data to model oil pipeline blockage problems.

2. Underpinning research (indicative maximum 500 words)

Research by Professor Steven Rowland's group at Plymouth University has been directed for 30 years, at improving knowledge of supercomplex mixtures of organic chemicals. These mixtures are of concern to environmental regulators (e.g. Environment Canada, EU) and wildlife agencies (e.g. RSPCA, RSPB) as important environmental pollutants and to industry (e.g. the oil industry in oil pipeline fouling).

Environmental legislation such as EU REACH regulations, aims to protect ecosystems, including humankind, from the toxic effects including cancer, of pollutant chemicals. However, legislation needs to be informed by science. The priority pollutants currently legislated for have excluded the orders of magnitude higher concentrations of unresolved pollutants (e.g., naphthenic acids) until recent awareness of Rowland's work (e.g., 'Monitoring oil sands toxicity': Chemistry World 16th March 2011). A significant shift in our research in the mid-1990s, initially with a widely cited, dual author paper in *Nature* in 1990, enabled Rowland (Professor of Organic Geochemistry Plymouth University, 1993-present) and successive PhD students (e.g. K. V. Thomas, PhD student 1992-1995, now Head of Ecotoxicology, NIVA, Norway) to develop research showing that extant environmental legislation ignored the importance of high concentrations of so-called 'unresolved complex mixtures' of pollutant chemicals. It was widely believed that the individual chemicals could not be identified; some considered the difficulty of identifying this 'petroleome' analogous to that of sequencing the human genome (A barrel load of compounds': Chemistry World, May 2010).

Professor Steven Rowland was convinced such mixtures could be resolved and showed with a prize-winning study at the World Congress of the Society for Environmental Toxicology and Chemistry (21-25 May 2000) by PhD student Emma Smith (now University of West Indies) and co-worker the late Dr Peter Donkin, that such mixtures were toxic to marine organisms and later with Tasman Crowe at University College Dublin, were even implicated in population effects on mussels. Rowland actively pursued this line of research, (as later, did scientists from, for example, the Wood's Hole Oceanographic Institution, USA), eventually receiving the first of a number of research contracts from the (then) Department of Environment, Transport & the Regions (DETR), the Maritime & Coastguard Agency and NERC in 1999-2004 to identify the toxicants, many of which resulted from crude oil degradation processes and were distributed worldwide.

Professor Rowland, along with the late Dr Peter Donkin who transferred from Plymouth Marine Laboratory to Plymouth University to work with Rowland, proceeded to show in a number of studies mainly that many of the toxicants could be identified and measured. The work resulted in international collaborative links with laboratories in Norway, Canada, USA, Australia and many others, in many cases with Plymouth as the lead partner (e.g. Maritime & Coastguard Agency Project 480 extension Potential Ecological Effects of Chemically Dispersed and Biodegraded Oils, 2005). Subsequently workers at Wood's Hole, Oceanographic Institution, USA, after discussion with Rowland, also pursued this avenue of research.

By 2006, Rowland, had developed an analytical method in collaboration with (then) Dr Ally Lewis at the University of York, based on multidimensional gas chromatography-mass spectrometry, which was capable of resolving the 'unresolved' mixtures and, with synthesis of the proposed chemicals,

Rowland was able to identify many of these and to demonstrate their toxicity to organisms such as mussels (e.g., Booth et al., 2007) and later (2013) in a internationally publicized chemical spill, to show the dramatic physical effects of man-made unresolved mixtures (e.g. polyisobutene) to seabirds.

In 2009 the importance of this work was recognised by a €2m Advanced Investigators Award by the European Research Council to Rowland who was then able to purchase a multidimensional gas chromatography-mass spectrometry system at Plymouth. The methods then allowed Rowland with samples supplied by Environment Canada, to identify the even more complex 'unresolved' toxic mixtures arising from the multi-billion dollar oil sands industries, which are the projected major supplier of USA crude oil for the next 50 years (e.g., Rowland et al., 2011a- c).

Rowland has now applied the methods to studies of airborne pollutant mixtures (e.g., Alam, M.S, West, C.E., Scarlett, A.G., Rowland, S.J. and Harrison, R.M. (2013) Application of 2D-GCMS reveals many industrial chemicals in airborne particulate matter. Atmospheric Environment 65, 101-111. [doi: 10.1016/j.atmosenv.2012.10.014]) and this promises to be important to human health impacts through inhalation as acknowledged by a recent 2m Euro Advanced Investigators Award by the European Research Council to Prof Harrison on which Rowland is a collaborator.

Most recently Rowland's team used the methods to identify a mystery spill of unresolved pollutant hydrocarbons (polyisobutenes), which killed thousands of seabirds along the south coast of the UK, leading to calls by public petition with thousands of signatures as well as from numerous agencies including the RSPCA and RSPB, to re-classify the hazards of the chemicals involved and several questions and ministerial and other statements in the UK parliament.

The industrial applications related to pipeline fouling resulted in grants of GB and PCT patents with patents pending in GB, USA and Canada (impacts of patents are given in Section 4 and listed in Section 5 below).

3. References to the research (indicative maximum of six references)

Details of selected recent publications by Professor Rowland in leading international journals in this area are given below (PU staff in bold):

1. **Rowland, S. J., West, C.E., Scarlett, A.G., Jones, D.,** Frank, R. and Hewitt L.M. (2011a).Steroidal aromatic naphthenic acids in oil sands process-affected water: structural comparisons with environmental estrogens. *Environmental Science & Technology* **45**, 9806- 9815.Peer reviewed. Impact Factor 5.257 May 2013
2. **Jones , D., Scarlett, A.G., West, C. E. and Rowland, S.J** (2011b) Toxicity of individual naphthenic acids to *Vibrio fischeri*. *Environmental Science & Technology* **45**, 9776-9782. Peer reviewed. Impact Factor 5.257 May 2013
3. **Rowland, S.J., Scarlett, A.G., Jones, D., West, C.E.** and Frank, R.A. (2011c) Diamonds in the rough: identification of individual naphthenic acids in oil sands process water. *Environmental Scence & Technology* 45, 3154. Peer reviewed. *This paper was also selected by the Editor-in-Chief to appear in a special online-only virtual issue entitled "Water- Energy Nexus" aimed at the scientifically literate general public.* Impact Factor 5.257 May 2013
4. **Sutton P.A., Smith, B.E.,** Waters, D. **and Rowland S.J.** (2010).Identification of a novel ester obtained during isolation of C80 ('ARN') tetraprotic acids from an oil pipeline deposit. *Energy & Fuels* 24, 5579-5585. Peer reviewed. Impact factor 2.853 May 2013
5. **Smith, B.E., Lewis, C.A., Belt, S.T.** Whitby, C. and **Rowland, S.J.** (2008) Effects of alkyl chain branching on the biodegradability of naphthenic acids. *Environmental Science & Technology* 42, 9323–9328. Peer reviewed. Impact Factor 5.257 May 2013
6. **A. Booth, P. A. Sutton, C. A. Lewis,** A. C. Lewis, **A. Scarlett, Wing Chau,** J. Widdows, **S. J. Rowland.** (2007). Aromatic hydrocarbons 'humps': thousands of overlooked persistent, bioaccumulative and toxic contaminants. *Environmental Science & Technology* 41, 457-464. Peer reviewed**.** *Featured on the ACS Publications website as one of the Most-Cited*

Articles published in ES&T in 2007. Impact Factor 5.257 May 2013

4. Details of the impact (indicative maximum 750 words)

The body of research undertaken by Prof Rowland and colleagues:

(a) is being used by oil companies such as BP, Chevron, Total and others to monitor and model oil pipeline problems,
(b) has significantly helped in enhancing the understanding of policy makers of environmental pollution from supercomplex mixtures of organic chemicals (e.g. Environment Canada) and
(c) has influenced public debate and engagement with scientific issues concerning maritime transport and spills of chemical pollutant mixtures (e.g. questions in UK parliament).

Applications arising from oil pipeline fouling have resulted in grants of a GB patent and PCT patents pending. A sophisticated computer model of oil pipeline fouling for a consortium including BP, Total, Chevron and others, is being developed by UK companies, InfoChem and OilPlus Ltd, using the analytical data provided by Rowland's team. Indirectly, all of these data benefit all those societies that use petroleum as an energy source. The methods are used routinely by Rowland's lab for a number of international oil companies on a regular basis (for example for high wax up to C100 compounds); much of this is, however, 'commercial in confidence' but can be provided on a confidential basis for audit purposes if required.

The environmental pollution issues have resulted in patents pending in GB, USA and Canada (as listed in Section 5 below). These are concerned with improved methods of pollutant monitoring developed by Rowland's team, particularly applicable in Canada. This helps to better address, for example, the call for the addition of unresolved mixtures of naphthenic acids pollutants to the National Pollutant Release Inventory in Canada (Proposal by Environmental Defence to Add Naphthenic Acids to the NPRI, available < http://www.ec.gc.ca/inrp-npri/default.asp?lang=en&n=AC708134-1> accessed 12 October 2012). Since issues with oil sands imports are also on the EU political agenda, in 2011 the European Environment Agency funded a lecture from Rowland on these and related emerging contaminants. The development and validation of the novel analytical methods has seen their uptake as the methods of choice by *Environment Canada* and for Rowland, funded visits and consultations by *Environment Canada* and the *Canadian Water Network* and presentations at numerous EU institutions including the *European Environment Agency* and the *European Centre for Environment & Human Health*. Professor Rowland's laboratory is recognised as the leading laboratory in the field of characterisation of unresolved pollutants including naphthenic acids, as endorsed by unsolicited statements by U.S. and Australian government non-academic scientists (Reddy, Wood's Hole, USA and Volkman, CSIRO Australia) in plenary lectures at international meetings in the EU and USA in 2011.

A written statement from an *Environment Canada* scientist confirms "*From the perspective of scientists such as myself and colleagues at Environment Canada, the research that Professor Steven Rowland's group at the Plymouth University has done into establishing methods to identify and measure complex mixtures of organic chemicals has had a significant impact on our understanding of the possible fate and effects of the multibillion dollar oil sands industries on the Canadian environment. The work provided the first real evidence of what naphthenic actually are – and has established which of the chemicals provide the most toxic threats to organisms, including fish. This topic is of immense public, political and sociological concern in North America, as demonstrated by press and TV, as well as more formal government reports*…."

Rowland's studies of unresolved pollutant mixtures allowed his team to identify two 'mystery' spills which killed thousands of seabirds in the UK in 2013. The substance was a polyisobutene (PIB) mixture. The information was of major assistance to the UK *Maritime & Coastguard Agency* and a senior Counter Pollution Officer has written to thank Rowland for his help. As a result of Rowland's findings, multi wildlife agencies, including the *Royal Society for the Protection of Birds* and the *RSPCA* have issued calls, supported by the UK *Chamber of Shipping*, to the *International Maritime Organisation* to review urgently the hazard classification of PIBs and to implement regulations that prevent any further incidents (e.g. http://www.bbc.co.uk/news/science-

environment-22505544; 13th May 2013). Meetings of the Bonn Convention partners in Europe have discussed the reclassification. The public weblog petition has received support from many thousands of U.K. citizens. The issue has received very high national and some international media coverage including in newspapers such as the *Guardian*, the *BBC* news and a BBC Inside Out documentary broadcast in September 2013. Also, the topic has been taken forward by MPs seeking a change in the law as well as by numerous environment groups and the UK Chamber of Shipping. Questions have been tabled in UK parliament and public statements by ministers have been made.

In short, methods developed by Rowland's team have proved useful for identifying and measuring thousands of previously unidentified industrial chemicals and toxic pollutants across the world; the 'petroleome' is at least partly, resolved.

5. Sources to corroborate the impact (indicative maximum of 10 references)

1. Statement of Research Scientist from *Environment Canada*, Government of Canada. This statement confirms the significant impact of Prof. Rowland's research on the understanding Environment Canada has of pollution from oil sands. It also confirms the immense public and political interest in this topic in North America.

2. Call by *Royal Society for Protection of Birds* for reclassification of polyisobutene as a result of Rowland's studies: http://portlandbirdobs.org.uk/pdf_PIB%20and%20seabirds%20RSPB%20Briefing%20revised%2014%20Feb%202013.pdf

3. Report in The Ecologist: http://www.theecologist.org/News/news_analysis/1809479/marine_pollution_incidents_kill_thousands_of_seabirds_and_it_could_be_legal.html

4. BBC National news**:** http://www.bbc.co.uk/news/uk-england-21350625

5. The Guardian Newspaper:

http://www.guardian.co.uk/environment/2013/feb/06/oil-additive-polymer-seabird-death

6. UK Patent granted: **Rowland, S.J & Smith B.E.** UK Patent: Publication number GB2447667.Application number GB0705299.6 Isoprenoid compounds, their isolation and use. Granted 2010.

7. UK Patent pending: **Rowland, S.J & Smith B.E.** (2008) International (Patent Cooperation Treaty) Patent: Application number PCT/GB2008/000976 Isoprenoid compounds, their isolation and use.

8. UK Patent pending: **Rowland S.J., West C.E., Scarlett A.G. and Jones D**. (2011) Method for the differentiation of alternative sources of naphthenic acids. UK Patent Application No. 1109838.1.

9. **Rowland S.J., West C.E., Scarlett A.G. and Jones D.** (2011) Method for the differentiation of alternative sources of naphthenic acids.Canadian Patent Application No. 2,743,156.

10. **Rowland S.J., West C.E., Scarlett A.G. and Jones D.** (2011) Method for the differentiation of alternative sources of naphthenic acids.U.S. Patent Application No. 13/160,367