Institution: University of Southampton		
Unit of Assessment: 07-05 Earth Systems and Environmental Sciences		
Title of case study: Difficult to measure (DTM) radionuclide characterisation supporting nuclear decommissioning and environmental monitoring		
Period when the underpinning research was undertaken: January 2000 – April 2019		
Details of staff conducting the underpinning research from the submitting unit:		
Name(s):	**Role(s) (e.g. job title):**	**Period(s) employed by submitting HEI:**
Phillip Warwick	Professor of Radioanalytical Chemistry	September 1994 – present
Ian Croudace	Professor Environmental Radioactivity and Geochemistry	March 1983 – July 2018
Andrew Cundy	Professor of Environmental Radioactivity	August 2016 – present
Pawel Gaca	Senior Radiochemist	January 2007 – present
Richard Marsh	Senior Research Fellow	October 2011 – July 2018; September 2020 – present
Period when the claimed impact occurred: August 2013 – July 2020		
Is this case study continued from a case study submitted in 2014? N		

1. Summary of the impact

Difficult-To-Measure (DTM) radionuclides pose a major challenge to nuclear waste characterisation, with decommissioning and environmental survey programmes being a significant contributor to radioactive inventories and requiring costly and time-consuming off-site specialist measurement. The University of Southampton (UoS) has developed knowledge, materials, methodologies, and hardware to facilitate more efficient and robust characterisation of DTM radionuclides in nuclear and environmental materials. Our work has delivered novel DTM radionuclide characterisation solutions to the nuclear industry (UK and internationally), and widespread adoption of our DTM methodologies by commercial and government end-users has extended capability to measure DTM radionuclides, facilitating decommissioning, improving efficiency in waste characterisation, and increasing assurance of data quality. Over the impact period, the adoption of our methodologies and technologies has generated over GBP3 million of enterprise income and at least GBP30 million in gross turnover for the UK economy.

2. Underpinning research

Characterisation of Difficult-To-Measure (DTM) radionuclides has been a long-standing (>20 year) focus of the UoS enterprise group GAU-Radioanalytical (**GAU**; formerly known as Geosciences Advisory Unit). The group has published over 48 papers relating to DTM characterisation since 2000. The underpinning research is divided into:

(a) Fundamental research into radionuclide-waste association: GAU has contributed significantly to the understanding of the physico-chemical behaviour of DTM radionuclides in nuclear wastes and its impact on sampling and analytical strategy. The research has extended knowledge of tritium (^{3}H) binding in metals as well as identifying, for the first time, the presence of multiple forms of ^{3}H in bioshield concretes [**3.1**]. When using conventional analytical approaches, this association may lead to severe underestimation of ^{3}H content, and therefore incorrect waste sentencing and disposal.

(b) Novel extractants/separation schemes: GAU have developed novel chromatographic materials for the extraction of a range of DTM radionuclides including ^{55}Fe, ^{99}Tc and $^{135/137}Cs$ [**3.2**]. These extraction chromatographic materials have been incorporated into novel rapid separation schemes, contributing to the understanding of DTM radionuclide separation science, and resulting in more efficient methodologies for DTM analysis. GAU were the first group internationally to develop a robust analytical separation scheme for ^{41}Ca, applying the technique to determine ^{41}Ca in a power-reactor bioshield concrete and demonstrating comparability between radiometric and accelerator mass spectrometric measurements [**3.3**]. This methodological breakthrough allows the use of the relatively straightforward, more cost effective and accessible liquid scintillation approach for quantifying ^{41}Ca activities during decommissioning programmes. Since 2013, Nuclear

Decommissioning Authority (NDA)-funded research has been undertaken into: (a) chromatographic theory underpinning DTM radionuclide separation and modelling of automated separation systems; and (b) rapid on-site screening of radionuclides based on test-stick technologies. These advances have paved the way to more rapid, automated separation schemes, and rapid on-site test systems to inform waste sentencing.

(c) Novel analytical procedures and measurement techniques: GAU have led in the development of analytical procedures for the determination of volatile radionuclides [**3.4**], including the design, testing and validation of a novel combustion Pyrolyser system (from 2003) for ^{3}H, ^{14}C, ^{36}Cl and ^{129}I determination, commercialised and marketed by the company Raddec Ltd (Directors Croudace and Warwick). In 2017, GAU was invited to collaborate with the National Physical Laboratory (NPL) and the NDA, to develop enhanced analytical hardware to enable its use in on-site/mobile laboratories to support decommissioning operations. In 2018, the application of the developed analytical hardware (the 'Pyrolyser Mini') to glove box operations in support of the Sellafield site decommissioning programme was undertaken. GAU have also led in the application of tandem mass spectrometry for the quantification of DTM radionuclides. Building on earlier work on the application of advanced mass spectrometry techniques for actinide analysis, and working with the NPL, the group has successfully demonstrated the application of inductively coupled plasma tandem mass spectrometry (ICP-QQQ) across a broad range of DTM radionuclides [**3.5**].

(d) Driving improvement to data quality: Through development of reference materials and contribution to nuclear data, GAU have driven significant improvements in data quality across the community. Under the co-ordination of the International Organically-Bound Tritium (OBT) Working Group, Croudace and Warwick (with Marsh) developed a chemically-stable OBT reference material [**3.6**]. For the first time, this then enabled analytical laboratories to validate their ^{3}H in soil data using ^{3}H in a known speciated form, allowing more reliable and robust environmental monitoring and risk assessment of ^{3}H around nuclear sites. Understanding of speciation is important as incorporation into organic materials significantly modifies tritium's behaviour in the environment and in humans.

3. References to the research

3.1 Kim D-J., Warwick P.E. & Croudace I.W., 2008. Tritium speciation in nuclear reactor bioshield concrete and its impact on accurate analysis. *Anal. Chem.,* **80**: 5476 – 5480. https://doi.org/10.1021/ac8002787

3.2 Russell B.C., Warwick P.E. & Croudace I.W., 2014. Calixarene-based extraction chromatographic separation of ^{135}Cs and ^{137}Cs in environmental and waste samples prior to sector field ICP-MS analysis. *Anal. Chem.,* **86**: 11890 – 11896. https://doi.org/10.1021/ac5036988

3.3 Warwick P.E., Croudace I.W. & Hillegonds D.J., 2009. Effective determination of the long-lived nuclide ^{41}Ca in nuclear reactor bioshield concretes: comparison of liquid scintillation counting and accelerator mass spectrometry. *Anal. Chem.,* **81**: 1901 – 1906. https://doi.org/10.1021/ac802225a

3.4 Warwick P.E., Kim D. Croudace I.W. & Oh J., 2010. Effective desorption of tritium from diverse solid matrices and its application to routine analysis of decommissioning materials. *Anal. Chim. Acta*, **676**: 93 – 102. https://doi.org/10.1016/j.aca.2010.07.017

3.5 Warwick P.E., Russell B., Croudace I.W. & Zacharauskas Z., 2019. Evaluation of inductively coupled plasma tandem mass spectrometry for radionuclide assay in nuclear waste characterisation. *J. Anal. At. Spectrom.,* **34**: 1810 – 1821. https://doi.org/10.1039/C8JA00411K

3.6 Warwick P.E., Croudace I.W., Marsh R.M., Baglan N. & Kim S-B., 2018. A new reference material for tritium organic molecules in sediment: results of an international intercomparison exercise. *Geostandards Geoanal. Res*., **42**: 253 – 262. https://doi.org/10.1111/ggr.12207

4. Details of the impact

Our core impact has been on practitioners (the nuclear industry and its supply chain), by extending industry capability to measure DTM radionuclides, improving the efficiency of waste characterisation, increasing assurance of data quality, and enhancing the nuclear skills base through training. The impact has been realised through: (a) extending industry capability to measure DTM radionuclides; (b) improving the efficiency of waste characterisation, in support of decommissioning and environmental programmes; (c) development and testing of DTM radionuclide-focussed analytical hardware and generation of technical data in support of routine hardware operation; (d) increasing assurance of data quality; and (e) provision of trained staff for the nuclear industry, in support of environmental and decommissioning programmes.

The development of improved methodologies, novel analytical procedures and quality control methods at UoS have benefitted the nuclear industry through GAU-Radioanalytical, a UoS enterprise group established in 1987 by Croudace. GAU is an ISO17025 accredited laboratory and is recognised as an international leader in radioactive waste characterisation. It has served the nuclear decommissioning sector since 1994, following the employment of Warwick. Significant improvements in analytical capability and throughput in the nuclear industry and its supply chain have been realised through the introduction of optimised DTM radionuclide characterisation methodologies and technologies, ultimately impacting on direct (analytical) and indirect (programme hold up, equipment hire, staffing, wastes sentencing etc.) project costs. All methodological and technical aspects have impacted significantly on the delivery of characterisation programmes in support of the nuclear and non-nuclear decommissioning programmes, fusion research and nuclear new build, as well as being adopted for environmental survey and research programmes. The technologies and methodologies that we have developed have had international reach. In the UK, the range of beneficiaries include nuclear industry decommissioning stakeholders requiring accurate and cost-efficient DTM radionuclide analysis (comprising 17 nuclear sites including Sellafield), UK regulators (Environment Agency), Culham Centre for Fusion Energy, GE-Healthcare sites (Cardiff and Amersham), nuclear submarine bases (Faslane, Rosyth and Devonport), AWE Plc, and the supply chain. Current estimates are that the UK's total radioanalytical market is worth approximately GBP22m per year of which analysis of DTM radionuclides represents approximately GBP15m per year. The adoption of our developed methodologies and technologies by GAU-Radioanalytical alone has facilitated DTM radionuclide characterisation programmes valued at GBP3,000,000 over the period 2014-2020 [**5.1**].

(a) Extending industry capability to measure DTM radionuclides. Our methodologies to measure the DTM radionuclides ^{3}H, ^{14}C, ^{41}Ca, ^{55}Fe, ^{63}Ni and actinides in a range of waste forms [**3.1**, **3.3**, **3.4**] have been transferred to commercial and government laboratories internationally, with knowledge transfer being facilitated through the development of industry-recognised training programmes and workshops. For example, following expert workshops in 2017 the India Centre for Advanced Research in Environmental Radioactivity adopted our ^{3}H and ^{14}C measurement technologies which are "*expected to significantly enhance… capability for monitoring and impact assessment of the environment and support the national capacity building*" [**5.2**]. Additionally, our published procedures and separation schemes for ^{3}H, ^{14}C, ^{41}Ca, ^{55}Fe, and ^{63}Ni, supported by site visits and training/knowledge transfer, have underpinned the development of new procedures at the Korean Atomic Energy Research Institute (KAERI) since August 2013, having a "*large impact on both KAERI [30% analytical time savings] and the delivery of the decommissioning programme in South Korea*" [**5.3**]. Knowledge transfer has also been realised via collaborative research (2015-2019) with NPL on the application of mass spectrometry (and in particular tandem mass spectrometry) for rapid radionuclide analysis. This has facilitated broader commercial application of the technique, which NPL "*have used for advancing forensic work and cross-group work for stable and radioactive isotope ratio measurement, as well as for isotope dilution mass spectrometry as part of improved nuclear decay data for long-lived radionuclides*" [**5.4**].

(b) Improving the efficiency of waste characterisation, in support of decommissioning and environmental programmes. UoS research has directly benefited practitioners by informing best practice in major decommissioning programmes including radiopharmaceutical facilities and sites belonging to the UK's first-generation nuclear fleet. The underpinning research also reduces project costs through avoidance of inappropriate or inefficient characterisation strategies and incorrect waste sentencing. Our research on the physico-chemical behaviour of ^{3}H in building and other materials [**3.1**] informed best practice in the decommissioning of the Cardiff Nuclear Licensed Site culminating in delicensing in 2019, with site operator GE-Healthcare noting that this work helped to "*prevent buildings being demolished at the site, as it enabled us to demonstrate that contamination was superficial and could be removed. This saved many tens of thousands of pounds*". In addition, our work developing methodologies for the robust assessment of the DTM ^{226}Ra in soils (2017-2018) allowed GE-Healthcare to build a credible, substantiated background figure for ^{226}Ra, which was accepted by the regulators. GE-Healthcare note that "*Without this work, and the subsequent regulatory agreement I am confident our remediation and delicensing work would have been almost impossible. This work was therefore critical in supporting the delivery of a multimillion-pound decommissioning project*" [**5.5**].

(c) Development and testing of DTM radionuclide-focussed analytical hardware and generation of technical data in support of routine hardware operation. The novel tube furnace combustion system for volatile radionuclides developed by GAU was commercialised as the Pyrolyser system (from 2003) and marketed by Raddec Ltd (a company with Directors Croudace and Warwick). This has enabled new business and supply chain opportunities and is estimated to have generated GBP30,000,000 to GBP40,000,000 in gross turnover in the UK economy. The Pyrolyser is established as the industry-standard device for extracting volatile radionuclides from any sample. In a recent international intercomparison exercise, 35% of the laboratories had adopted the Pyrolyser system over conventional technologies for environmental ^{3}H analysis [**3.6**]. In the decommissioning sector the percentage of laboratories using the Pyrolyser is even higher, with all five laboratories contracted to support the UK Low Level Waste Repository Waste Characterisation and Assurance Support Services (WCASS) programme (adopted by Low Level Waste Repository Ltd. (LLWR), Magnox and Research Sites Restoration Ltd. (RSRL) to support their waste characterisation requirements) operating Pyrolyser systems. Worldwide, the hardware and methodologies have been adopted to support nuclear and environmental analytical programmes in 14 countries including Ireland (EPA – Dublin), France (Eichrom), Belgium (SCK-CEN), Sweden (Studsvik, FOI), the Netherlands (RIKILT, NRG), Romania (Cernavoda NPP), China (Xi'an Accelerator Mass Spectrometry Centre), South Korea (KAERI, KRISS, KINS, KHNP), USA (JNL, GEL, PNNL, SRNL), India (BARC, CARER) and Canada (CNSC). Since 2014, over 40 systems have been installed, representing an impact on commerce and the economy valued at approximately GBP1,500,000 with over 80% as export.

Development of the Pyrolyser Mini system in 2017-2018 has extended the application of the system for higher activity and hazardous materials, further expanding the capability of the system, increasing commercial/economic impact and providing significant additional functionality for practitioners. During its development, the Pyrolyser Mini system was assessed as a nuclearized technology in support of the Sellafield Ltd decommissioning programme [**5.6**]. This is a key illustration of our impact on decommissioning, as the Sellafield site represents one of the biggest technical and environmental challenges faced by the UK. The current expected cost of the UK's nuclear legacy facilities is GBP119billion, however the Nuclear Decommissioning Authority (NDA) has estimated that it could cost in the region of GBP97billion to GBP222billion over the next 120 years, with Sellafield taking almost 75% of the annual budget. The Sellafield Central Lab Facility is the biggest new investment in analytical infrastructure in the UK. Sellafield Ltd recognise that game-changing technologies such as those developed by our group are required to deliver the Site's target end-state and a key part of the decommissioning process includes accelerating analytical throughput for effective waste characterisation (especially for Intermediate Level Wastes). In rising to meet the challenge of developing 'nuclearized' instrumentation, Sellafield Ltd noted that our "*purpose designed enhanced Pyrolyser system will meet the demanding requirements specified including undertaking multiple types of analysis in a hot cell environment in support of the decommissioning of the Sellafield site*" [**5.7**]. The UK Government has recently announced GBP86,000,000 for fusion research to set up a national fusion technology platform at the UK Atomic Energy Authority's Culham Science Centre in Oxfordshire. Tritium is a critical fuel for planned thermonuclear reactors and Pyrolyser technologies are already targeted as a requirement for operational support. Currently 3 Pyrolyser systems are located at the Culham site. One Pyrolyser system has recently been acquired to determine total ^{3}H in metallic samples to corroborate the effectiveness of the Site's recently established Materials Detritiation Facility. This facility is estimated to have saved more than GBP1,000,000 in disposal costs through improved wastes characterisation, with UKAEA noting "*The Pyrolyser system and associated expertise is key to providing characterisation capability underpinning this programme*". [**5.8**]

(d) Increasing assurance of data quality. Since 2012 GAU's Croudace & Warwick have participated in the Scientific Committee of the International Organically-Bound Tritium (OBT) Working Group, including specialists drawn from nuclear organisations in Canada, China, France, India, Japan, Romania, UK (e.g., those using PWR, HWR, CANDU and fusion reactors). The Group is concerned with developing radioanalytical protocols/standards and OBT reference samples to support laboratories undertaking research and ^{3}H contamination measurements around reactor sites. The OBT reference material developed and characterised by Warwick et al. [**3.6**] has been used in proficiency testing to enable analytical laboratories to validate their ^{3}H in soil data using ^{3}H in a known speciated form for the first time. This has resulted in more robust procedural validation with a member of the OBT working group organising committee stating that "*The production of an OBT reference sediment by the University of Southampton's GAU-Radioanalytical enterprise group and subsequent testing by 27 laboratories in 9 countries through the 2014 intercomparison exercise has improved data quality and end-user confidence in ^{3}H measurements*" [**5.9**]. This in turn has allowed environmental monitoring and risk assessment programmes to incorporate more accurate assessments of ^{3}H mobility and health risks around nuclear sites.

(e) Provision of trained staff for the nuclear industry, in support of environmental and decommissioning programmes. Fourteen PhD students have contributed to the DTM radionuclide characterisation research programme (7 since August 2013), 10 of whom have gone on to work in related industry. Many organisations have benefitted from participation in training programmes and workshops held in the UK (Babcock International Group, AWE, Tradebe), Denmark (covering Scandinavian participants), South Korea and India. Tradebe noted "*this training on radionuclide characterisation, DTM measurement techniques and research developments is seen as essential to improve the characterisation of radioactive waste materials as a vital precursor to its safe and cost-effective management in the UK and overseas*" [**5.10**]. In 2019, the group was awarded a GBP1,200,000 EPSRC grant (PI Warwick, co-I Cundy, grant number EP/T011548/1) to establish and operate a National Nuclear Users Facility for radioactive waste characterisation research and technology development, reflecting the group's strong track record in R&D and training, with a core component of providing training for the academic and commercial sector in *in-situ*, on-site and off-site characterisation and remediation methods.

5. Sources to corroborate the impact

5.1 Summary of GAU-Radioanalytical commercial performance relating to DTM analysis.

5.2 Testimonial from the India Center for Advanced Research in Environmental Radioactivity.

5.3 Testimonial from the Korean Atomic Energy Research Institute.

5.4 Testimonial from the National Physical Laboratory, UK.

5.5 Testimonial from GE-Healthcare.

5.6 Sellafield Ltd. – nuclearized Pyrolyser development. 'Study into the use of a combined furnace unit in radioactive analytical cells. Kirvan S. Sellafield Ltd. Presented at the Royal Society of Chemistry 13th International Symposium on nuclear and environmental radiochemical analysis. 17th – 20th September 2018, Cambridge, UK.

5.7 Testimonial from Sellafield Ltd.

5.8 Testimonial from the Culham Centre for Fusion Energy.

5.9 Testimonial from the International OBT working group.

5.10 Testimonial from Tradebe Inutec.