Research Assessment Exercise 2020
Impact Case Study

University: City University of Hong Kong
Unit of Assessment (UoA): 9 Chemistry

Title of case study: Managing risks of per- and polyfluoroalkyl substances (PFASs)

(1) Summary of the impact

Our work raised environmental awareness and defined new sensitive analytical methodology of per- and polyfluoroalkyl substances (PFASs). Techniques for trace analyses of PFASs were developed in key environmental matrices, contributing to the International Harmonization of analytical methods for PFASs;

Our research influenced policy and legislation globally through providing key evidence relating to the distribution and persistence of PFASs. Global transport pathways of PFASs (especially non-volatile PFASs) were elucidated, making clear their environmental processes and impacts;

Status and trends information was used to manage the production and use of legacy and emerging PFASs by global international institutions/agencies (e.g. UN, UNEP, WHO).

(2) Underpinning research

My research team has been instrumental in developing analytical methods for PFASs in key environmental matrices (e.g. air, water, sediment, and biological samples) **[1-6]**. When we started analytical work on PFASs in 2003, there were several limitations to the detection and quantification of these compounds **[1]**. One of the most severe limitations was the high level of background interference, which came from the fact that PFASs are to be found in many laboratory appliances and cause contamination of not only samples, but also laboratory reagents. This contamination could come from everything from the septa used in auto-sampler vials, to internal parts of the high-performance liquid chromatography instruments (HPLC). We found that to conduct analyses of PFASs with desirable Limit of Quantifications, a number of internal parts on a standard HPLC-mass spectrometry (HPLC/MS) had to be modified. For example, substituting stainless steel or peek tubing and other components for Teflon® in all parts of the instrument including the inlet filter. Finally, we successfully developed a solid phase extraction-HPLC-tandem MS (SPE-HPLC-MS/MS) procedure to measure PFASs at parts-per-trillion (ng/L) levels in seawater **[1, 3]**. Later, these sensitive and reliable analytical methods were extended to a wide range of biological samples **[2]** [Environ. Sci. Technol. (ES&T). 40:3736-41].

Analysis of PFASs in environmental samples had, initially, focused on a relatively small group of compounds for which quantification methods were available. My research team successfully developed a method to measure both the total fluorine (TF) and the amount of organic fluorine extractable using existing methods in a sample [referred to as the extractable organic fluorine (EOF) fraction] (J. Chromat. A. 1143:98-104 and 1154:214-21; ES&T 42:8140-45). By using this method in combination with established procedures for measuring individual "known" PFASs, the concentrations and relative proportions of "known" PFASs and "unknown" PFASs with regard to EOF could be determined, as well as the proportion of TF that was comprised of EOF (ES&T 42:8140-45). My data indicated that only around 10-30% of the EOF in environmental samples was comprised of “known” PFASs **[6]**. These findings have subsequently led to the development of an active field of research on non-targeted analysis of PFASs in the environment.

Furthermore, approximately 10 individual Indo-Pacific humpback dolphins and finless porpoises are stranded in Hong Kong waters annually. My research team has been collecting cetacean stranding samples (blubber and liver tissues) since 2002. Sample information (including year of collection, sex, size, developmental stage, and cause of death) was recorded for each individual whenever possible. Over the past decade or so, a small “specimen bank” of samples from these marine mammals has been established in my laboratory. The archived samples provided a unique opportunity for us to elucidate the contamination status and temporal trends of legacy and emerging PFASs in the Pearl River Delta region (ES&T 50: 6728-36), which remains one of the fastest-growing manufacturing hubs in the world. These studies are important in revealing the emergence and impact of replacement chemicals as and when the use and production of existing chemicals are restricted or banned.

(3) References to the research

[1] So, M.K., Taniyasu, S., Yamashita, N., Giesy, J.P., Zheng, J., Fang, Z., Im, S.H. and Lam, P.K.S.*, 2004. Perfluorinated compounds in coastal waters of Hong Kong, South China and Korea. Environ. Sci. Technol. 38: 4056-4063. (ISI Web of Science Citation: 289)
[2] So, M.K., Yamashita, N.*, Taniyasu, S., Jiang, Q., Giesy, J.P., Chen, K. and Lam, P.K.S.*, 2006. Health risks in infants associated with exposure to perfluorinated compounds in human breast milk from Zhoushan, China. Environ. Sci. Technol. 40: 2924-2929. (ISI Web of Science Citation: 208)
[3] Yamashita, N.*, Taniyasu, S., Petrick, G., Wei, S., Gamo, T., Lam, P.K.S. and Kannan, K., 2008. Perfluorinated acids as novel chemical tracers of global circulation of ocean waters. Chemosphere 70: 1247-1255. (ISI Web of Science Citation: 184)
[4] Taniyasu, S., Kannan, K.*, Yeung, L. W. Y., Kwok, K. Y., Lam, P. K. S. and Yamashita, N.*, 2008. Analysis of trifluoroacetic acid and other short-chain perfluorinated acids (C2–C4) in precipitation by liquid chromatography–tandem mass spectrometry: Comparison to patterns of long-chain perfluorinated acids (C5-C18). Anal. Chim. Acta 619: 221-230. (ISI Web of Science Citation: 109)
[5] Mak, Y.L., Taniyasu, S., Yeung, L.W.Y., Lu, G.H., Jin, L., Yang, Y.L., Lam, P.K.S.*, Kannan, K. and Yamashita, N.*, 2009. Perfluorinated compounds in tap water from china and several other countries. Environ. Sci. Technol. 43: 4824-4829. (ISI Web of Science Citation: 171)
[6] Loi, E.I.H., Yeung, L.W.Y., Taniyasu, S., Lam, P.K.S.*, Kannan, K. and Yamashita, N.*, 2011. Trophic magnification of poly- and perfluorinated compounds in a subtropical food web. Environ. Sci. Technol. 45: 5506-5513. (ISI Web of Science Citation: 114)

(4) Details of the impact

My research team has developed sensitive, reliable, and robust analytical methods for emerging chemicals of concern, in this case PFASs, in key environmental matrices. In 2004, we developed a SPE-HPLC-MS/MS procedure to measure PFASs at parts-per-trillion (ng/L) levels in seawater. This study revealed for the first time the widespread occurrence of PFASs in Chinese and Korean waters (Environ. Toxicol. Chem. 25:2374-80). Further studies revealed the occurrence of PFASs in Chinese rivers (Chemosphere 68:2085-95), surface waters between Asia and Antarctica (Mar. Poll. Bull. 54:1813-18), and open oceans (Chemosphere 70:1247-55). In 2008, we developed a liquid chromatography–tandem mass spectrometry method to analyze short-chain PFASs (Anal. Chim. Acta 619:221-30). These results demonstrated the ubiquitous distribution of PFASs in the global environment, which laid part of the foundation for the standardized determination methods

(HELCOM, ISO) **[A, B]**. Our work is recognized by Dr. Heidelore Fiedler, former Team Leader of the Science and Risk Team at the Chemicals Branch of the United Nations Environment Programme (UNEP). Support letter is given in **[G]** of part (5).

Contribution to the water monitoring guidelines issued by UNEP. Importantly, my analytical method was sensitive enough for measuring PFASs in open ocean waters. We then participated in a global study, which yielded important data lending strong support to the hypothesis that non-volatile PFASs were transported to polar regions via ocean currents (Chemosphere 70:1247-55). Our sensitive and selective method enabled the trace analyses of PFASs in ice core, surface snow and water samples collected from Norwegian Arctic. As glaciers were formed by the compression of fallen snow over many years, the glaciers sampled, located at high altitude, was expected to receive PFAS contamination mainly from atmospheric pathways. Therefore, ice cores in this location was used to investigate the transport pathways of PFASs and provide information on the temporal trends of atmospheric concentrations of PFASs. Melted glacier water further reflected atmospheric and local PFAS contamination from over several years, while surface snow and water samples represented recent sources from both local and global sources. Our results comprehensively demonstrated the atmospheric transport of PFASs over and above the pathway via ocean currents (Sci. Total Environ. 447:46-55). Collectively, our research contributed to the water monitoring guidelines issued by UNEP (2015) **[C]**.

Development and validation of analytical methods for determination of PFASs in biological samples. Using the analytical method developed by my research team, concentrations of PFASs were analysed in seafood (ES&T 40:3736-41) and in human blood (ES&T 40:715-20), as well as human breast milk samples (ES&T 40:2924-29) collected from China. One important finding was that the daily intake of certain PFASs for the child exceeded the predicted conservative reference dose, indicating that there may be potential risk of certain PFASs for the infants via the consumption of breast milk in China. In 2007, my research team published two papers on the determination of total fluorine in water and blood samples (J. Chromat. A. 1143:98-104 and 1154:214-21). Using this method, my research team demonstrated that the PFASs being targeted for scientific investigation and/or environmental surveillance at that time actually represented only a very small fraction (around 10-30%) of extractable organofluorine compounds in the environment. Recently, these findings raised widespread interest in the search for “unknown PFASs” among researchers in this field in order that a more comprehensive/meaningful risk assessment of organofluorine compounds can be conducted.

Assessment of the environmental and public health risks of PFASs. We studied the toxic effects of PFASs in rats (Toxicol. Sci. 89:93–107); chickens (Toxicology 237:111-25); and on primary cultured fish hepatocytes (Aquat. Toxicol. 82:135-43). Following on from these, we successfully developed methods for measuring PFASs in bird eggs (ES&T 42: 8146-51) and cetacean tissues (Environ. Poll. 157:17-23; ES&T 50:6728-36); as well as in tap water (ES&T 43:4824-29). More recently, we have studied the trophic biomagnification of PFASs in a wetland food web (ES&T 45:5506-13) and examined the health effects to humans through the consumption of aquatic foods. Taken together, these studies contributed to the health advisory opinions issued by several authorities, such as World Health Organization, Health Canada, United States Environmental Protection Agency, and OECD **[D-F, H-J]**.

Phasing out of the legacy PFASs has resulted in compensatory production and usage of alternatives, such as shorter- or longer-chain PFASs, and other structurally similar PFASs. These emerging PFASs are inevitably released into the environment. Our research has been concerned with the status and trends as well as the environmental impact of legacy and emerging PFASs. The information collected was used to manage (e.g., setting exposure limits or guideline values) or instigate a ban, if warranted, on the production and use of these chemicals by Global International Agencies (e.g., United Nations Environment Programme, World Health Organization) **[D-F, H-J]**.

(5) Sources to corroborate the impact

[A] ISO/DIS 21675 Water quality (2019) -- Determination of polyfluorinated alkyl substances (PFAS) in water -- Method using solid phase extraction and liquid chromatography-tandem mass spectrometry (LC-MS/MS). (Listed in the Bibliography)

[B] HELCOM (Baltic Marine Environment Protection Commission - Helsinki Commission) (2018) Guideline on the determination of Perfluoroalkylated substances (PFAS) in seawater. (e.g. Page 4)

[C] Weiss, J., de Boer J., Berger U., Muir, D., Ruan, T., Torre, A., Smedes, F., Vrana, B., Clavien, F., Fiedler H. (2015). PFAS analysis in water for the Global Monitoring Plan of the Stockholm Convention. Set-up and guidelines for monitoring. Chemicals Branch, United Nations Environment Programme (UNEP), Division of Technology, Industry and Economics, Geneva, Switzerland. (e.g. Pages 3, 4, 6, 18, 20, 29)

[D] WHO (World Health Organization)/UNEP (United Nations Environment Programme) (2013). The State-of-the-Science of Endocrine Disrupting Chemicals – 2012 (Bergman Å, Heindel JJ, Jobling S, Kidd KA, Zoeller RT, eds). Geneva: UNEP/WHO. (e.g. Pages: 86, 145, 203, 211-214, 220-221)

[E] Health Canada (2016). Perfluorooctane Sulfonate (PFOS) in Drinking Water. Document for Public Consultation Prepared by the Federal-Provincial-Territorial Committee on Drinking Water, Canada. (e.g. Pages 7, 10, 28)

[F] Health Canada (2016). Perfluorooctanoic acid (PFOA) in Drinking Water. Document for Public Consultation Prepared by the Federal-Provincial-Territorial Committee on Drinking Water, Canada. (e.g. Pages 7, 10, 12)

[G] Support letter written by Dr. Heidelore Fiedler, former Team Leader of the Science and Risk Team at the Chemicals Branch of the United Nations Environment Programme (UNEP).

[H] New Jersey Drinking Water Quality Institute Health Effects Subcommittee (2017). Health-based maximum contaminant level support document: perfluorooctanoic acid (PFOA). New Jersey Drinking Water Quality Institute, USA. (e.g. Pages 30, 39)

[I] United States Environmental Protection Agency (2016). Drinking Water Health Advisory for Perfluorooctanoic Acid (PFOA). Office of Water (4304T), Health and Ecological Criteria Division, Washington, DC 20460, USA. (e.g. Page 25)

[J] OECD (2013). OECD/UNEP Global PFC Group, Synthesis paper on per- and polyfluorinated chemicals (PFCs), Environment, Health and Safety, Environment Directorate, OECD. (e.g. Page 24)