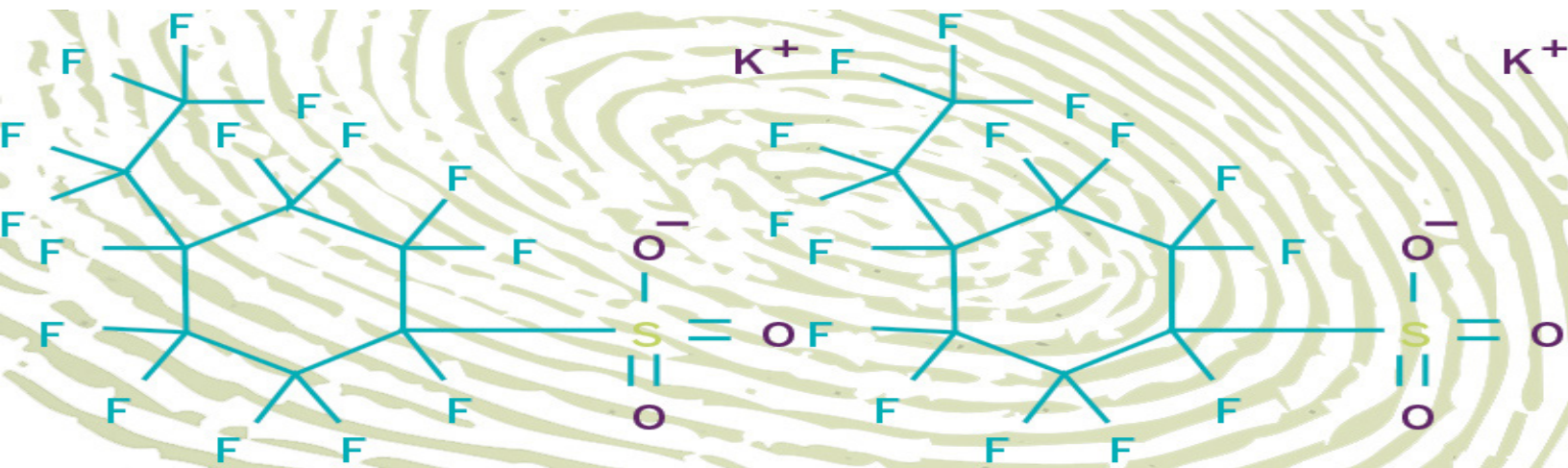




Forensic chemistry differentiates PFAS sources



Chemical fingerprinting proves PFOA found upgradient did not originate from historical use of military specific AFFF at a former fire training facility.

Site scenario

Near former fire training and aqueous film forming foam (AFFF) storage areas, we conducted a site investigation to collect and analyze soil, sediment and groundwater samples. Compounds detected in soil and sediment samples were typical of those known to be present in historical perfluorooctane sulfonic acid (PFOS) military specific AFFF formulations used until about the year 2000. Groundwater samples were found to contain much higher perfluorooctanoic acid (PFOA) concentrations over PFOS concentrations. These concentrations were also found upgradient of the fire training areas, where Per- and Polyfluoroalkyl Substances (PFASs) were not expected to be present. PFOA is not a historically documented ingredient in military specific AFFF products, and the presence and distribution of PFOA in site groundwater suggested an unknown source distinct from the fire training areas.

Response

We relied on site history, historical AFFF formulations and knowledge of PFAS chemistry to perform a forensic evaluation to determine possible sources of PFOA at the site. We concluded that

operations and use of the fire training areas ended in or before 1992, so only PFOS-based AFFF formulations were used by the client. The current property owner constructed a new hangar with fire suppression systems upgradient of the fire training areas in 2006.

After the year 2000, AFFF manufacturers changed the composition from a PFOS-based formulation to one based on fluorotelomer sulfonates (FTSs). FTSs are synthesized via a mechanism that leads to nearly 100% linear isomer composition, while historically manufactured PFOS and PFOA contain a mixture of linear and branched isomers. It is now known that FTSs can be biologically or abiotically degraded to form corresponding perfluorocarboxylic acids (PFCAs), and that one FTS (8:2-FTS) degrades to form PFOA.

Amec Foster Wheeler chemists examined the ion profiles from the site to determine whether the composition of the PFASs detected included a mixture of linear and branched isomers, or only linear isomers. This evaluation showed that all perfluoroalkyl sulfonates detected, including PFOS, consisted of a mixture of linear and branched isomers. Detected

PFCAs, however, consisted exclusively, or nearly exclusively, of the linear isomer, consistent with PFCAs derived from degradation of FTS-based AFFF. The chemical composition of the PFCAs therefore corroborates the information about site history, AFFF compositional history and the distribution of PFOA in groundwater at the site. The multiple lines of evidence demonstrated that PFOA in environmental media at the site is related to AFFF handled at the site after cessation of our client's operations and use of the fire training areas.

The evaluations showed that the PFOA present in site groundwater was related to AFFF formulations that could not have been used by our client during their tenure at the site, and the client was not responsible for further investigation of PFOA at the site. Negotiations with other stakeholders continue. The chemical forensic technique applied here may be generalized to PFASs from sources other than AFFFs. As applied for this purpose, the fingerprinting evaluation was roughly equivalent to homolog-based fingerprinting of PCBs. The technique can be extended by working with labs to increase chromatographic resolution

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and monitoring additional fragmentation reactions for each compound. Given the large number of industrial applications of fluorinated surfactants, source differentiation is likely to grow in importance along with regulatory scrutiny. Though development of PFAS-specific forensic techniques are in their infancy, the basic principles of chemical forensics of this compound class are similar to those applied to other complex mixtures such as PCBs, PAHs, and TPH.

PFOA - Note single peak from linear isomer

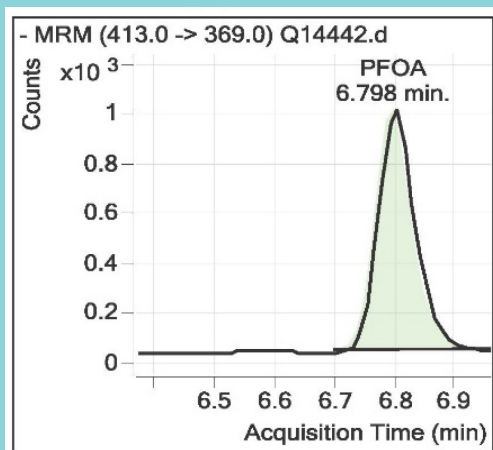


Figure 1: Ion current profile for PFOA showing a single peak that corresponds to the linear isomer only, consistent with FTS-based manufacturing methods.

PFOA - Note peaks for branched/linear isomer

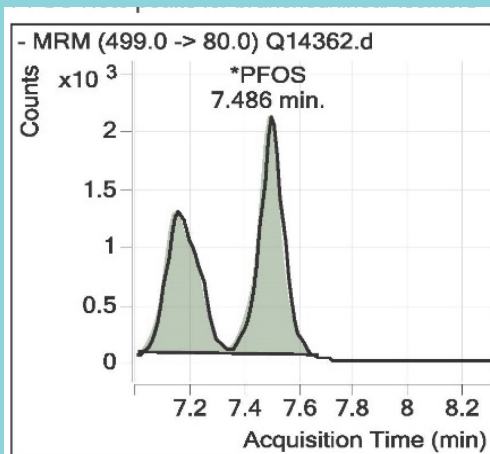


Figure 2: Ion current profile for PFOA, showing 2 peaks that correspond to branched isomers (left peak) and the linear isomer (right peak) consistent with older electrochemical fluorination (ECF) manufacturing methods.