

# DIRECT INJECTION ANALYSIS BY SUPERCRITICAL FLUID CHROMATOGRAPHY COUPLED TO TANDEM MASS SPECTROMETRY OF TRIFLUOROACETIC ACID IN WATER CONNECTED TO SUSPECTED POINT SOURCES

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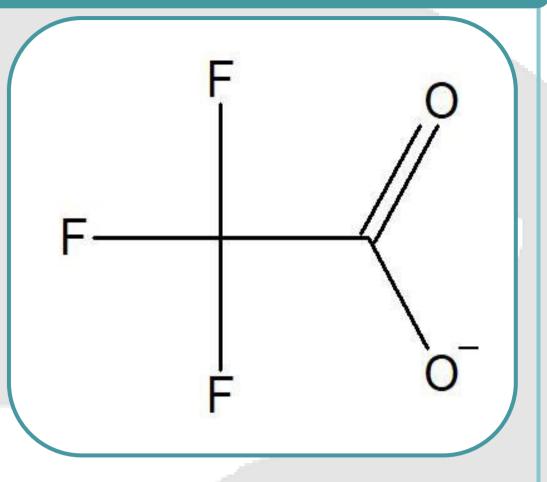


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## Introduction

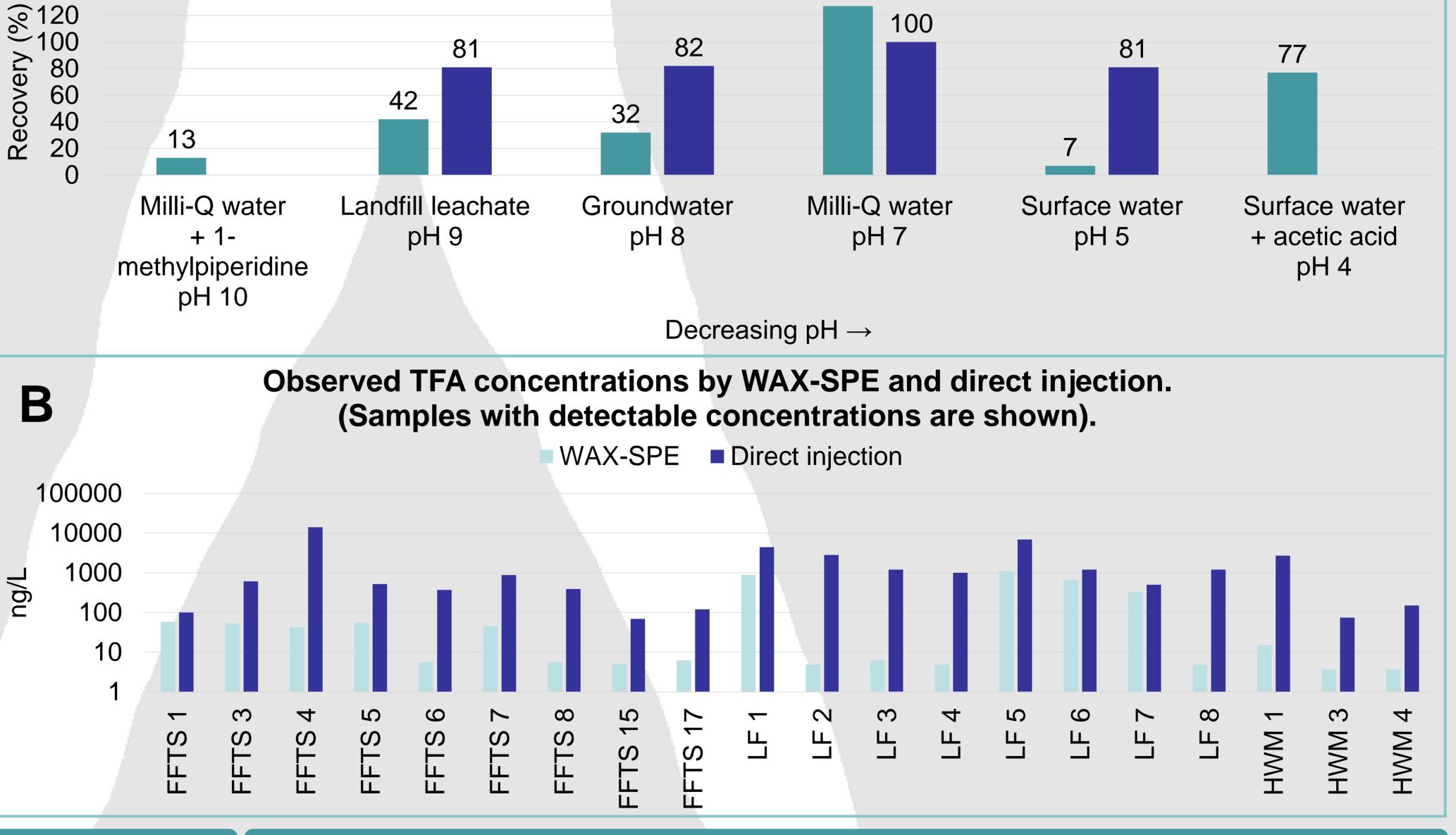
Trifluoroacetic acid (TFA) is a persistent perfluoroalkyl acid (PFAA) found globally. Concentrations of TFA have been frequently reported in various environmental matrices including precipitation, surface water, groundwater and air. One well-known source of TFA is the atmospheric degradation of hydrofluorocarbons and hydrochlorofluorocarbons. However, other sources, some of which are not known, may play a relevant role in the high concentrations being observed in the environment. Extraction of TFA from water samples has been frequently done by weak anion exchange solid-phase extraction (WAX-SPE). However, analysis of TFA is often obstructed by elevated blank concentrations and mass labelled standards are not commonly used. Semi-quantification of TFA using mass-labelled perfluorobutanoic acid (PFBA) as internal standard that are added to the sample prior to extraction with WAX-SPE may result in over- or underestimation of TFA concentrations due to different extraction- and ionization efficiencies of TFA and PFBA. In this study, a method based on direct injection analysis with supercritical fluid chromatography (SFC) was applied for the determination of TFA in water samples (*n*=33) connected to suspected point sources in Sweden. The recoveries of spiked test samples and the measured concentrations of TFA were



### compared between the direct injection method and the WAX-SPE method.

### Sample preparation and analysis $^{13}C_4$ -PFBA (IS) $^{13}C_3$ -PFBA (RS) SFC-MS/MS 5-500 mL Evaporation SFC-MS/MS · Xevo TQ WAX-SPE WAX-SPE Water sample SFC-MS/MS **Direct injection** 250 µL 250 µL MeOH + ${}^{13}C_4$ -PFBA (IS) Results Recovery (%) of TFA based on the signal of TFA spiked to test samples • The recovery of TFA by WAX-SPE varied from 7 to 42% compared to the signal of TFA spiked in solvent A (Figure A). WAX-SPE Direct injection The recovery of the direct injection was $81 \pm 0.4\%$ . 140 127

- $(19 \pm 0.4\%$  ion suppression).
- The recovery of TFA by WAX-SPE did not seem to be related solely to the pH of the sample but the combination of the pH and sample matrix.
- The concentrations of TFA observed with direct injection was up to 600 times higher compared to concentrations observed with WAX-SPE (Figure B).
- The detection frequency of TFA in in the 33 samples was 61% by direct injection and only 30% by WAX-SPE.
- TFA was detected in 20 out of 33 samples (by direct injection) at concentrations ranging from <34 to 14 000 ng/L (median concentration 110 ng/L).</li>
- The highest concentration of TFA (14 000 ng/L) was found in water from a rock shelter with previous usage of AFFF in sprinkler systems.
- TFA was generally more frequently detected at higher concentrations in landfill leachate (<34-6 900 ng/L) indicating that leaching from landfills may be a relevant source for TFA into the environment.



### Conclusions

### TFA in water connected to suspected point sources (results by direct injection)

- The recovery of the direct injection method only suffered from ion suppression while the recovery of the WAX-SPE method seem to be be dependent on several factors incluing pH and sample matrix causing losses during sample extraction.
  WAX-SPE resulted in an underestimation of TFA due to losses during sample preparation that are not compensated for by using mass labelled PFBA.
  Firefighting training sites, landfills and hazardous waste management facilities may me relevant sources for TFA to the environment.
  - Analysis by direct injection was shown to be an adequate method for measuring TFA in samples from point sources.

#### Sample matrix and sample description Concentration range (ng/L) Firefighting training sites Groundwater and surface water collected at and <34-14 000 20 downstream of five sites with known usage of AFFFs. Landfill storm water and leachate collected at three <34-6 900 9 different landfills. <34-2 700 Surface water collected at the outlet and management facility (HWM) downstream from a hazardous waste management facility.

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