

# 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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## Introduction

Trifluoroacetic acid (TFA) is a highly persistent compound found globally. Levels of TFA have been reported in precipitation (<0.1-2 400 ng/L),<sup>1,2</sup> in surface water (<0.5- 140 000 ng/L),<sup>1,3</sup> and in ocean water (1-230 ng/L).<sup>4</sup> One well-known source is the atmospheric degradation of hydrofluorocarbons and hydrochlorofluorocarbons used as cooling agents.<sup>5</sup> Another source of TFA is the thermolysis of fluoropolymers.<sup>6</sup> High concentrations of TFA have been observed in municipal (90-600 ng/L) and industrial (<100-206 000 ng/L) wastewater effluents<sup>7</sup> and in surface water downstream a chemical production industry (5 400-140 000 ng/L).<sup>3</sup> Trifluoroacetic acid is also used as a laboratory chemical<sup>8</sup> and it is a degradation product of hydrofluorocarbons used in fire extinguishers.<sup>9</sup> However, other sources may also play an important role in the occurrence of high concentrations of TFA in the environment. Large variations in recovery of TFA during extraction by weak anion exchange solid-phase extraction (WAX-SPE) have been observed and reported recently.<sup>10</sup> In the present study, a method based on direct injection analysis with supercritical fluid chromatography (SFC) was applied for the determination of TFA in water connected to suspected point sources in Sweden. The method was compared to a method based on WAX-SPE for validation of the recovery of the method. Spearman rank correlations was calculated to investigate correlations between TFA and other PFASs.

## Materials and methods

### *Chemicals and reagents*

Trifluoroacetic acid was purchased from Sigma-Aldrich, Munich, Germany (98% purity). Pure mass-labelled standard for TFA was not available. Mass labelled standard for perfluorobutanoic acid (PFBA) was from Wellington laboratories Guelph, ON, Canada. Glass microfiber filters (Whatman), was purchased from Sigma-Aldrich, Stockholm, Sweden. Ammonia solution (NH<sub>4</sub>OH) and methanol were from Fischer Scientific, Ottawa, ON, Canada. Weak anion exchange solid-phase extraction (WAX-SPE) cartridges were obtained from Waters Corporation, Milford, MA, USA.

### *Sampling*

Water samples ( $n=33$ ) were collected at and around suspected point sources in Sweden. Samples were collected from five firefighting training sites (FFTSs) ( $n=20$ ), three municipal and industrial landfills (LF) ( $n=9$ ) and downstream a hazardous waste management facility (HWM) ( $n=4$ ). The FFTSs are sites with a known usage of aqueous film forming foams (AFFFs) and include two rock shelters equipped with sprinkler systems with AFFFs. All samples were collected in polyethylene containers that had been rinsed with Milli-Q water and methanol prior to sampling. All samples were stored refrigerated (+8 °C) until processing.

### *Sample preparation and analysis*

Analysis of TFA was performed by direct injection of filtered water samples after 1:1 dilution in methanol to a final volume of 0.5 mL. The same water samples were also analyzed after extraction of 5-500 mL water by WAX-SPE following the ISO25101 method. Test samples were spiked with native TFA standard and treated according to the same protocol as both of the described methods for evaluation of method recovery. Separation and quantification was performed using SFC coupled to tandem mass spectrometry (MS/MS) operated in negative electrospray ionization mode. Separation was achieved on a SFC DIOL column (3.0 mm i.d., 150 mm length, 1.7 μm particle size, Waters Corporation, Milford, MA, USA). The mobile phase consisted of CO<sub>2</sub> (A) and 0.1% NH<sub>4</sub>OH in methanol (B). A gradient program was used starting at 2% B, increased to 60% over 8 min, held for 1 min and finally returned to initial conditions in 1 min. The flow rate was initially 1.3 mL/min and decreased to 0.8 mL/min over 8 min, held for 1 min and then increased to 1.3 mL/min in 1 min. The active back pressure regulator

was set to 1 500 psi. A make-up flow of methanol was added to the split of the SFC before coupling to the MS/MS and was set at 0.5 mL/min. The source parameters were set as following: Capillary voltage, 0.7 kV; source temperature, 150 °C; desolvation temperature, 400 °C; cone gas flow, 150 L/h; desolvation gas flow, 800 L/h; collision gas flow, 0.2 mL/min; nebulizer, 6.5 bar. The MRM transition monitored for TFA was m/z 113 to m/z 69 and the cone voltage and collision energy was -30 V and 5 eV, respectively. Other transitions were not observed.

### ***Quality assurance and quality control***

A pure mass labelled standard for TFA was not available at the time of analysis. Quantification of TFA was performed by isotope dilution using mass labelled PFBA as internal standard and the results are therefore semi-quantitative.

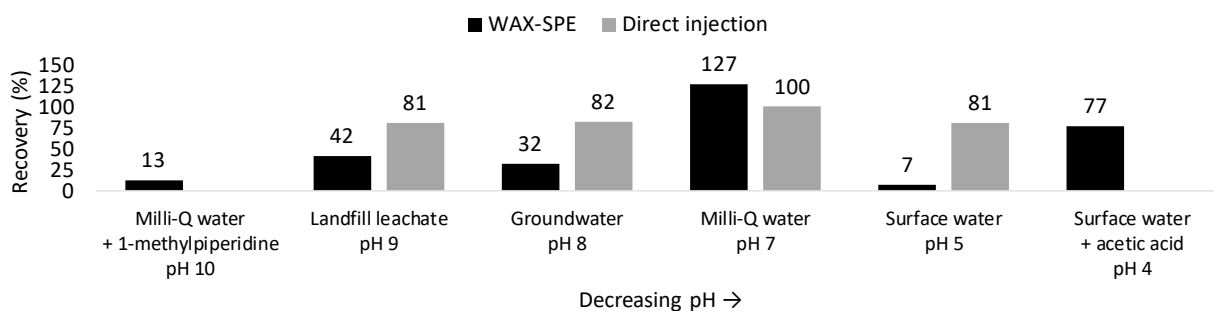
During direct injection analysis there was a constant background signal for TFA from the SFC-MS/MS system. Therefore data obtained by direct injection is reported after blank subtraction from the instrument. The method limit of detection (MDL) and the method quantification limit (MQL) was defined as three and ten times the standard deviation of repeated blank direct injections ( $n=4$ ) consisting of Milli-Q water:methanol (1:1, v/v). Ion signal effects during direct injection analysis were assessed by spiking 2 ng native standard to selected test samples ( $n=3$ ). Non-spike test samples were spiked with an equal volume of methanol. Ion signal effects were then evaluated by comparing the peak area of spiked test samples with a standard after subtraction of the peak area in non-spike test samples. Ion matrix suppression on TFA observed during electrospray ionization was  $19 \pm 0.4\%$ . Ion matrix suppression on PFBA was  $4 \pm 11\%$ . The difference was not compensated for.

During sample extraction with WAX-SPE, three blank extractions were included in each batch of samples. The MDL and MQL were calculated as the average concentration in the blank plus three or ten times the standard deviation, respectively. Data is reported without blank subtraction. The extraction efficiency (WAX-SPE) and analytical performance were evaluated based on test samples ( $n=3$ ) spiked with native TFA standard after subtraction of the background concentration in the test samples. The pH of the samples was recorded prior to extraction. The recovery of TFA was  $27 \pm 18\%$ . The recovery of PFBA was  $76 \pm 23$ . The difference was not compensated for.

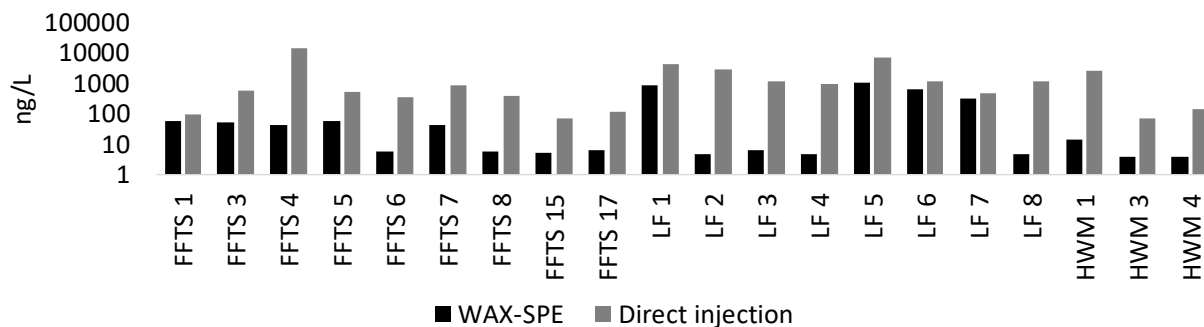
## **Results and discussion**

### ***Direct injection analysis versus solid-phase extraction for analysis of trifluoroacetic acid in water***

The recovery of TFA by WAX-SPE varied from 7 to 42% in three selected test samples (landfill leachate, groundwater and surface water) (Figure 1). The recovery did not seem to be related solely to the pH of the sample but rather the combination of the pH and sample matrix. Addition of 1-methylpiperidine to Milli-Q water to increase the pH resulted in a decrease in recovery from 127 to 13%. Addition of acetic acid to the surface water sample to decrease the pH increased the recovery from 7 to 77%. These results may be explained by ion-pair formation between TFA and basic compounds that are broken up upon addition of an acid. Strong ion-pair formation between TFA and basic compounds are formed when TFA is used as a mobile phase additive for chromatographic separation of basic compounds causing signal suppression during mass spectrometric determination.<sup>8</sup> The same set of test samples (excluding Milli-Q water with addition of 1- methylpiperidine or acetic acid) were used to evaluate the recovery (due to ion signal effects) of the direct injection method. The recovery of the direct injection method with the test samples was  $81 \pm 0.4\%$  (Figure 1). The concentrations of TFA in the water samples observed by WAX-SPE versus direct injection are shown in Figure 2. The observed TFA concentrations by WAX-SPE were up to 600 times lower (sample LF 2) than the concentrations observed by direct injection. In addition, the detection frequency of TFA in in the 33 samples was 61% by direct injection and only 30% by WAX-SPE. These results clearly illustrates the drawbacks of WAX-SPE for the analysis of TFA in water samples when no mass labelled internal standard is used.



**Figure 1.** Recovery (%) of TFA during WAX-SPE (black) and direct injection (grey).



**Figure 2.** Concentrations of TFA observed after extraction by WAX-SPE (black) and direct injection (grey). Only samples in which TFA was detected above the MDL with at least one of the methods are included.

### Trifluoroacetic acid in water connected to suspected point sources

Quantification of TFA was performed by direct injection analysis by SFC-MS/MS. Concentration range and description of the different sample sites are given in Table 1. Trifluoroacetic acid was detected in 20 out of 33 samples analyzed at concentrations ranging from <34 ng/L to 14 000 ng/L (median 121 ng/L). The highest concentration of TFA was observed in outflowing water from a rock shelter with previous usage of AFFF in sprinkler systems, consisting of a mixture of groundwater, storm water and surface water. This may suggest that TFA is present in the AFFF as a byproduct, or as a degradation product of short- and long-chain PFASs. Furthermore, TFA is a degradation product of 2H-heptafluoropropane (HFC-227ea) used in fire extinguishers.<sup>9</sup> High concentrations were generally observed in water collected in connection to landfills. The concentrations observed in landfill leachate ranged from below the MDL (<34 ng/L) to 6 900 ng/L (median 1 200 ng/L) with a detection frequency of 89%. This suggest that leaching from landfills is a relevant source for TFA to the environment.

**Table 1.** Concentration of TFA (ng/L) and a description of sample matrix and the sampling sites included.

Site	<i>n</i>	Sample matrix and sample description	Concentration range (ng/L)
Firefighting training sites (FFTSs)	20	Groundwater and surface water collected at and downstream of five sites with known usage of AFFFs.	<34-14 000
Landfills (LFs)	9	Landfill storm water and leachate collected at three different landfills.	<34-6 900
Hazardous waste management facility (HWM)	4	Surface water collected at the outlet and downstream from a hazardous waste management facility.	<34-2 700

High concentrations of TFA were observed in samples collected at one site with known usage of AFFFs. At this site, samples were collected on two occasions. The TFA concentration was one order of magnitude higher during the second sampling occasion (sample FFTS 4) than in a sample collected at the same location three months earlier (sample FFTS 3). This was also true for other PFASs measured in the same samples (C4-C12 PFCAs, C2-

C12 PFASs, 6:2-FTSA and 8:2-FTSA). This considerable increase of TFA along with the increase of other abundant PFASs indicate that the source of TFA at this site may be of the same origin as for the other PFASs, i.e. the use of AFFFs. Although, the increase in concentrations varied from one to four orders of magnitude among different target PFASs. The increase from the first to the second sampling occasion was relatively small for TFA (one order of magnitude) compared to other PFASs (up to four orders of magnitude) and could be a result of higher mobility of shorter-chain compounds.

Spearman rank correlations were calculated to investigate correlations between TFA and other PFASs. Two samples collected after treatment with granular activated carbon was excluded since the relative concentration of TFA and other PFASs has been altered. Only samples in which TFA was detected above the MDL were included ( $n=18$ ). Correlations were observed between TFA and C4-C9 perfluoroalkyl carboxylic acids and 6:2 and 8:2 fluorotelomer sulfonic acids ( $r>0.7$ ,  $p<0.01$ ). These compounds and TFA were generally found in higher concentrations in water collected in connection with landfills.

The observation of high concentrations TFA in water connected to different types of suspected point sources reveals the diversity of possible sources of TFA to the environment. Furthermore, the correlations observed between TFA with other PFASs suggest that TFA may (in addition to other sources) originate from the same type of sources as other PFASs, possibly as a byproduct and/or degradation product of short- and long-chain PFASs.

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