DETERMINATION OF PCDD/FS AT FG/L LEVEL IN SPRING WATER SAMPLES COMPARED TO MAIN WATER

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Introduction

Spring water is recognised to be a safe source of drinking water worldwide. This kind of water is continuously subject to conformity tests involving almost all known pollutants. We have been asked to determine PCDD/Fs concentrations in spring water by a provider of such product. His aim was not to verify that all congeners were below usual detection limit, but he wanted to know how much dioxins and furans were actually present in the water. The challenge, beyond the analysis of PCDD/Fs itself, was to set up a pre concentration device in order to sample a large amount of water, to decrease the detection limits below the pg/l, as requested by our customer.

Material and Methods

Solvents were purchased from LGC Promochem – Molshein – FRANCE
Adsorbents (silica gel, alumina, anhydrous sodium sulphate) were purchased from VWR - FRANCE
Amberilte XAD-2 was purchased from SUPELCO - FRANCE

100 litres of each spring water sample were directly brought to our lab by the provider.

Main water was collected from the tap from a source close to the lab, in 20 L cleaned glass bottle with silanized surface.

We designed a pre concentration device, based on absorption of PCDD/Fs on a resin Amberlite XAD-2 traditionally used to sample PCDD/Fs from stack emissions [1]. This apparatus was home made in high quality glass, deactivated by silanisation of in order to avoid adsorption of non-polar compounds such as PCDD/Fs on the glass surface (figure 1). The water was flowing through the resin (flow rate : 100 ml/min), retaining compounds of interest; the cartridge was filled with 10 g of specially purified resin.

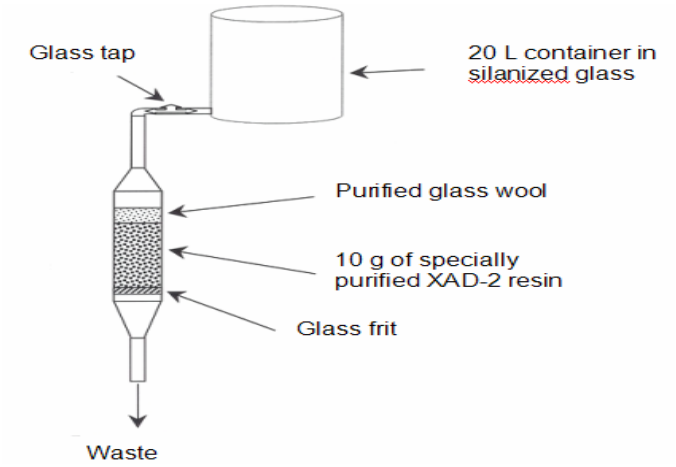

Figure 1 : not on scale, experimental pre concentration apparatus

Then, the XAD-2 resin was were spiked with 15 isotopically labelled dioxins and furans (480 pg for the tetras, pentas and hexas, and 960 pg for the heptas and octas) before overnight air drying under a fume hood in order to

eliminate water. XAD-2 was subsequently solid-liquid extracted in a Soxhlet by using toluene as extraction solvent for 24 hours (4-6 cycles per hour).

The extract was then purified following EPA 1613A method [2]:

A silica column: (from top to bottom, 1 g of anhydrous sodium sulphate, 1 g of activated silica, 8 g of 30 % sulphuric acid impregnated silica, 1 g of activated silica, 4 g of 23 % sodium hydroxide impregnated silica). The PCDD/Fs were isolated from the extract by eluting this column with n-hexane.

A basic alumina column (from top to bottom, 1 g of anhydrous sodium sulfate, 15 g of activated basic alumina, activity I). A first fraction eluted with n-hexane/methylene chloride (98:2, v:v) was discarded. A second fraction, eluted with n--hexane/methylene chloride (1:1, v:v) was collected and concentrated.

Just before HRGC/HRMS analysis, purified extracts were reconstituted by adding 20µl of a standard solution containing ^{13}C 1,2,3,4 TCDD and ^{13}C 1,2,3,7,8,9 HxCDD (480 pg of each added to the extract) to monitor recoveries achieved during the HRGC/HRMS analysis.

The levels of PCDD/Fs in the water extracts were determined using HRGC/HRMS on an Autoconcept. The Autoconcept is a high resolution double focusing mass spectrometer of EB geometry produced by Mass Spectrometry Instruments Ltd. (MSI), Manchester, UK. The system is directly coupled to a high resolution gas chromatograph (HP6890, Agilent Technologies) fitted with a split/splitless injector. The mass spectrometer was operated at a resolution of 10000 (10% valley definition). The source was operated at a temperature of 250°C with an electron voltage of 30eV at a trap current of 300uA.. The capillary column for GC separation was J&W DB 5 MS, 60m length, 0,25mm internal diameter and 0,25µm film thickness. The identification criteria specified in USEPA Method 1613 [2] with respect to the GC column performance and mass spectrometer performance were fully satisfied by the data obtained in this study (separations, resolution and sensitivity capabilities).

Results and discussion

Determination of recovery rate of labeled compounds with volume of water through XAD-2 resin

First, we determined the ability of the XAD-2 cartridge to retain labeled PCDD/Fs to optimize the volume of water we could apply at once to the system.
We fortified 5 water samples (from 10L to 50L, steps of 10L) with known amounts of ^{13}C PCDD/Fs. These 5 water samples were applied to 5 XAD-2 cartridges which were subsequently analyzed as describes in previous part.

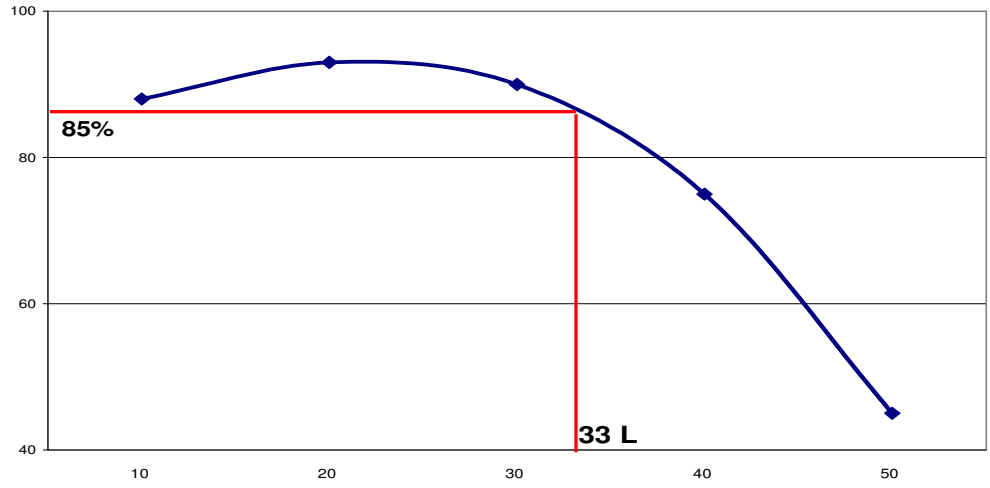

Figure 1 : Mean recovery rate of PCDD/Fs compared to water volume through the resin cartridge

The figure 1 shows that for 33 L eluted from the column, the mean recovery rate for the labeled congeners was 85 %, which is convenient to sample 100 L of water in three steps. The recoveries are slightly better for smaller amounts of water, but the full experiment would have been much more complicated to achieve by collecting resin after pre concentration of less than 20 L of water.

Specially purified batch of resin

In order to determine sub pg/l levels, we specially prepared a batch of XAD-2 resin, extensively purified by Soxhlet extraction with toluene, for more than one full week. The concentration of PCDD/Fs in such resin was determined by a blank of procedure (repeated three times), including every preparation step, from air drying to analysis by HRGC/HRMS. The mean concentration was equivalent to 0,32 fg/l TE WHO PCDD/Fs. This corresponds to 30 g of resin (three times 10 g, 10 g is used to pre concentrate 33 L of water). No congener was detected. The 0,32 fg/l TE WHO PCDD/Fs value is upperbound as every other concentration presented here.

Sampling and analysis of spring waters

The two different spring waters were applied to the pre concentration device in three times of 33 L each, on a 10 g XAD-2 extra purified resin. The flow rate was approx 100 ml/min, taking days to pre concentrate one sample.
We sampled main water in parallel, to compare the concentrations of PCDD/Fs.
Figure 2 shows the TE WHO PCDD/Fs in fg/l upperbound for the blank, the two spring waters and the main water. The main water is the most "contaminated" sample with 64 fg/l WHO PCD/Fs, but the level is far away from the usual levels found in drinking water in France [3] which are usually around 1000 fg/l TEWHO PCDD/Fs. Besides, the results presented here are a lot below Ontario's standards for dioxin in drinking water (15 pg/l TE WHO PCDD/Fs) [4].

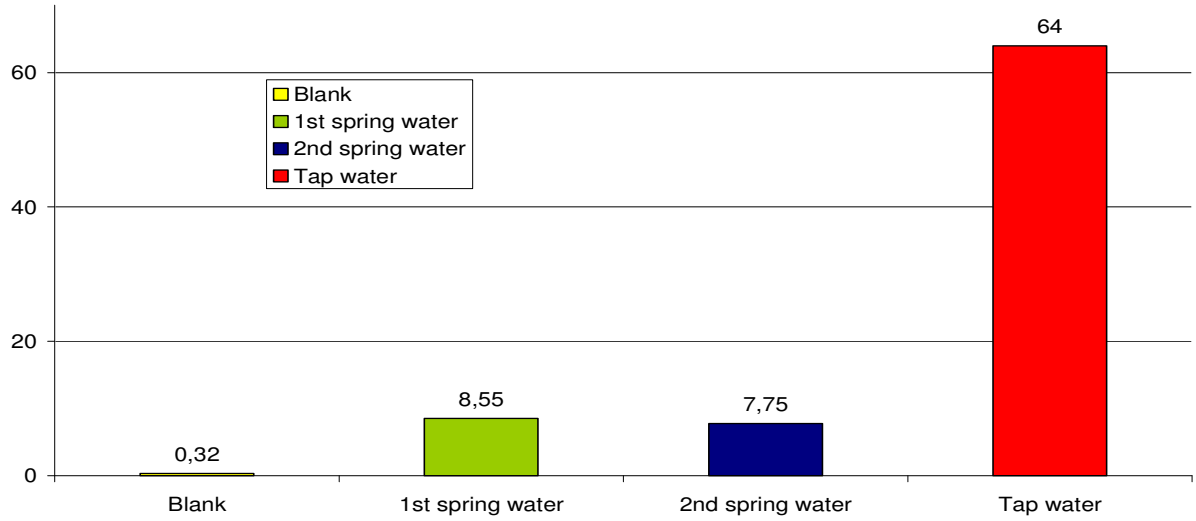

Figure 2 : TE (upperbound) PCDD/Fs WHO fg/l

Figures 3 and 4 display the profile of congeners for PCDD and PCDF respectively.

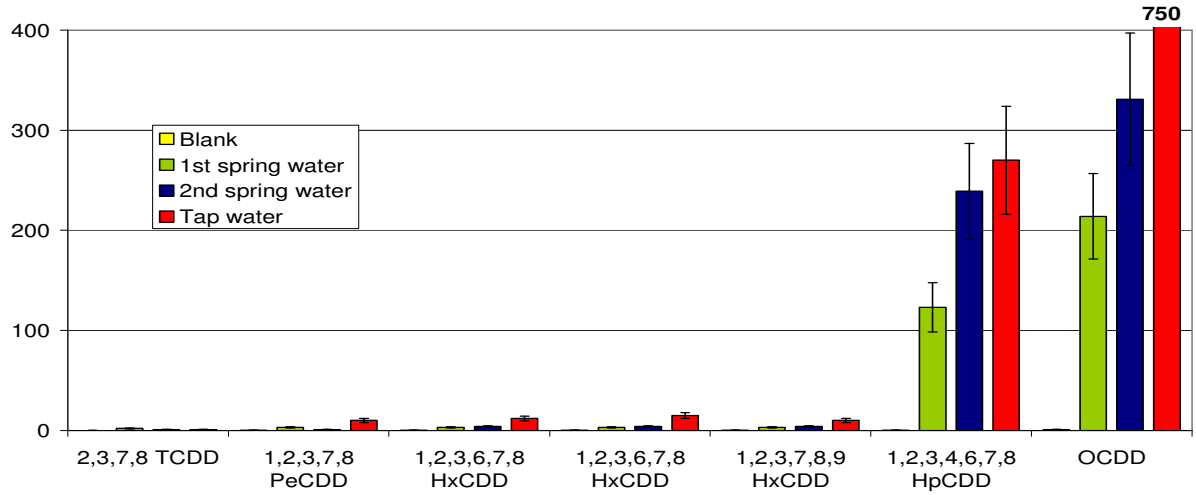

Figure 3 : PCDD concentrations (fg/l) in different samples

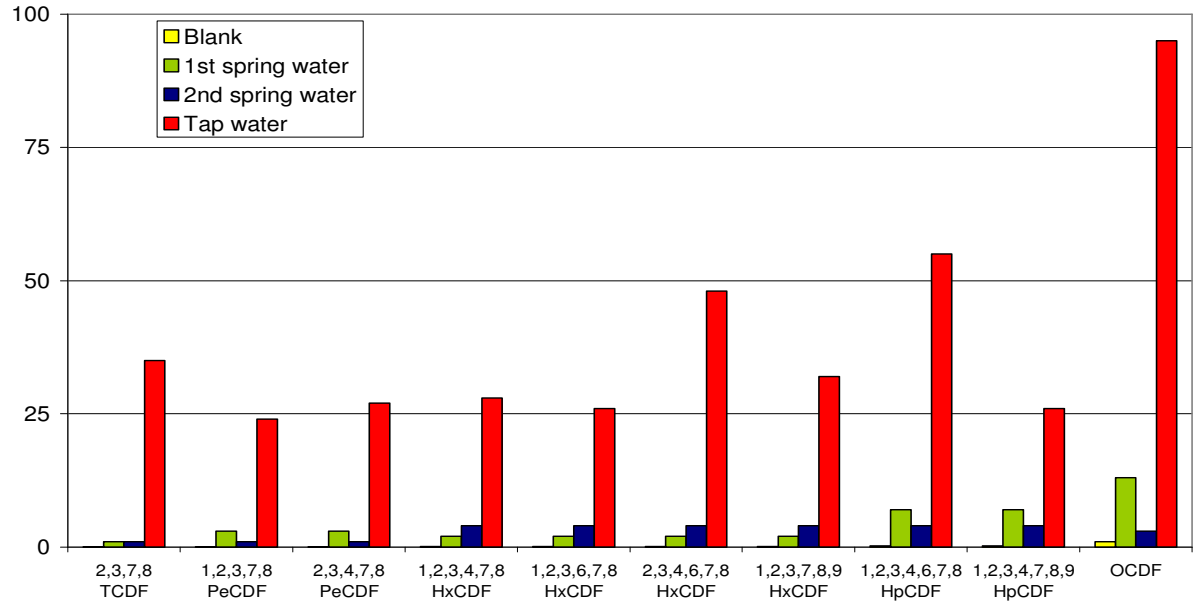

Figure 4 : PCDF concentrations (fg/l) in different samples

Whereas only highly chlorinated dioxin congeners are found in main water, all furans congeners are found. The level of those contaminants in spring waters remains very low in comparison. Highly chlorinated dioxins are usually found is a vast majority of environmental or water samples. Furan contamination (which is still very low) contributes to the total TE for about 80 % of the total TE for tap water.

Conclusion

This study shows that spring water is very slightly contaminated by highly chlorinated dioxins only at fg/l level, whereas main water from local source is about 10 times more contaminated. However, the concentrations found in all types of water in this study remain largely below know recommended values and are below usual values

found in other studies. The challenge was to be able to quantify fg/l levels of dioxins and furans in water samples, and not only to assess that all congeners were found below limits of detections by using 1 L of sample. This have been achieved by designing a home made device to pre concentrate a large volume of water on specially purified absorbent resin XAD-2, usually used to sample PCDD/Fs from stack samples.

Bibliography

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[3] AFSSA Saisine N° 2003-SA-0305 : http://www.afssa.fr/Ftp/afssa/29308-29309.pdf

[4] Ontario standard for dioxin in drinking water : http://www.ene.gov.on.ca/cons/681e01.htm