

PCDD/F AND PCB ANALYSIS OF DRINKING WATER IN THE ATTOMOLE RANGE

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Abstract

High volume sampling (50-100 m³) of drinking water quality of water allowed the detection of PCDD/F and PCB in the fg/L range. The performance of the sampling procedure was reassured employing sampling standards and resulted in proper recoveries. Pattern of analytes of two different water sources differentiate them clearly in quality and quantity. The pattern indicate mobility due to water solubility of the compounds as well as potential transfer of HpCDD and OCDD possibly carried with (nano-)particulates.

Introduction

Together with emerging exploration of surface near groundwater to provide the population with drinking water it becomes more and more important to develop insight into the presence of POP in drinking water resources (cite WFD). Thus, a major task directly linked to this is the screening of aquifers for 'future' contaminants, *i.e.* contaminants which today are present in only low concentrations often below general detection limits and regulation thresholds but exhibiting clear increasing trends. Here, we head for an early warning concept to be prepared for tomorrow's groundwater management issues.

Methods to elaborate concentrations of contaminants from large volumes of groundwater will help to identify tomorrow's contaminants of concern.

Small and persistent molecules are most likely to enter the human pathways and are therefore of major concern to interfere with biological signal systems. Many trace pollutants with such properties (e.g toxic elements, pesticides, antibiotics, BFR, PFC, POPs etc.) being potentially present in groundwater systems for drinking water purposes are in the focus of the related investigations with relevance for impacts on humans and their resources. Many lipophilic POP are not believed to penetrate through the soil column into groundwater systems. However the current limits of determination for drinking water are adjusted to sample volumes of about 1 L. The analytical tools are not capable to check LOD far below one tenth of the current limits which is not sufficient to achieve the abovementioned goals. Thus it became necessary to develop novel tools to meet the goals. First attempts and results about this purpose are reported.

Materials and Methods

Materials. All used solvents were of trace analysis grade and supplied by LGC Standards (Wesel, Germany), as well as the silica and alumina adsorbents. The ¹³C-labeled standards were purchased from LGC Standards or Campro Scientific (Berlin, Germany). The XAD resin (Supelpak 2) was acquired from Sigma (Taufkirchen, Germany). The activated charcoal (granular) was purchased from VWR (Ismaning, Germany). Both, the XAD resin and the charcoal were solvent extracted before use to reduce possible blank values.

Sampling Procedure. The sampling system consisted of four trap units connected directly in series. In flow direction the first two units were filled with 40 g XAD and topped with glass wool, respectively. Labeled sampling standards for PCDD/F and PCB (composition according to DIN EN 1948) were spiked on top of the first one. The third and fourth unit contained a layer of 20 g of activated charcoal, respectively. The system was connected to the water tap by a flexible stainless steel tube. A water meter was installed at the outlet. The water flow rate was in the range of 0.1 to 0.2 m³ h⁻¹.

Water from two different sources was sampled. One source was the regional drinking water system, the other water originated from a groundwater well on the campus of the research center. The latter was used for technical cooling purposes and was not treated in any way. Replicate sampling campaigns (2 or 3) were performed. The time span between each campaign was about 2 month.

Sample Preparation and Instrumental Analysis. The cartridges filled with XAD were extracted in a Soxhlet

apparatus for 24 h with a mixture of n-hexane/acetone (3:1 v/v). The activated carbon layers were extracted separately by use of pressurized liquid extraction (ASE 200, Dionex) with toluene.

The sample preparation and instrumental analysis was performed according to El-Kady et al.². In brief, a multicolumn clean-up was applied to the samples using sulfuric acid treated silica, activated carbon, alumina and C18-modified silica as adsorbents. The prepared samples were analysed by GC/HRMS (MAT95S, Thermo Scientific) using an Rtx-Dioxin2 capillary column for PCDD/F and an Rtx-CLPesticides2 for PCB.

Results and Discussion

The recoveries of the sampling standards are shown in Table 1. They are all in a satisfying range for the high amount of water passed through the sampling unit. However, in many cases they are above 100% which is partly a result of the fact that in total 4 subunits are investigated for their single recoveries. Especially the last sampling units contain only minor amounts of the sampling standards below 10% which might contribute to the total overestimation. In many cases the last trap unit does not contain analytes and confirms the quantitative trapping of the analytes of interest.

Table 1: Recoveries of sampling standards employed for high volume drinking water sampling

Sample	Drinking water	Drinking water	Drinking water	Well water	Well water
Volume	101 m ³	125 m ³	87 m ³	55 m ³	52 m ³
1,2,3,7,8-PeCDF- ¹³ C ₁₂	98%	130%	103%	137%	79%
1,2,3,7,8,9-HxCDF- ¹³ C ₁₂	83%	98%	95%	82%	98%
1,2,3,4,7,8,9-HpCDF- ¹³ C ₁₂	68%	99%	97%	99%	99%
PCB #60- ¹³ C ₁₂	96%	80%	123%	69%	80%
PCB #127- ¹³ C ₁₂	107%	106%	106%	161%	129%
PCB #159- ¹³ C ₁₂	82%	90%	110%	91%	108%

The concentrations of the WHO-TEQ (Table 2) are found in the attogram per liter range and many of the contributing compounds could be clearly identified in the two different drinking water resources. The blank values are significantly below the presented values. Interestingly the two different water sources exhibit also clear differences in their concentrations whereas the values within the replicates are quite similar. The values found here are very different from values of drinking water reported by Zielinski et al.³. The reason might be the difference in sampling volume by a factor of more than 100000. Large sampling volumes are more protective against analytical artifacts and laboratory background situations.

Table 2: WHO-TEQ of repeated water sampling of two German drinking water sources

Sample	Drinking water	Drinking water	Drinking water	Well water	Well water
Volume	101 m ³	125 m ³	87 m ³	55 m ³	52 m ³
	ag/L	ag/L	ag/L	ag/L	ag/L
PCDD/F-TEQ	260	220	130	60	< 0.1
PCB-TEQ	480	530	350	10	< 0.005
Total	740	750	480	70	

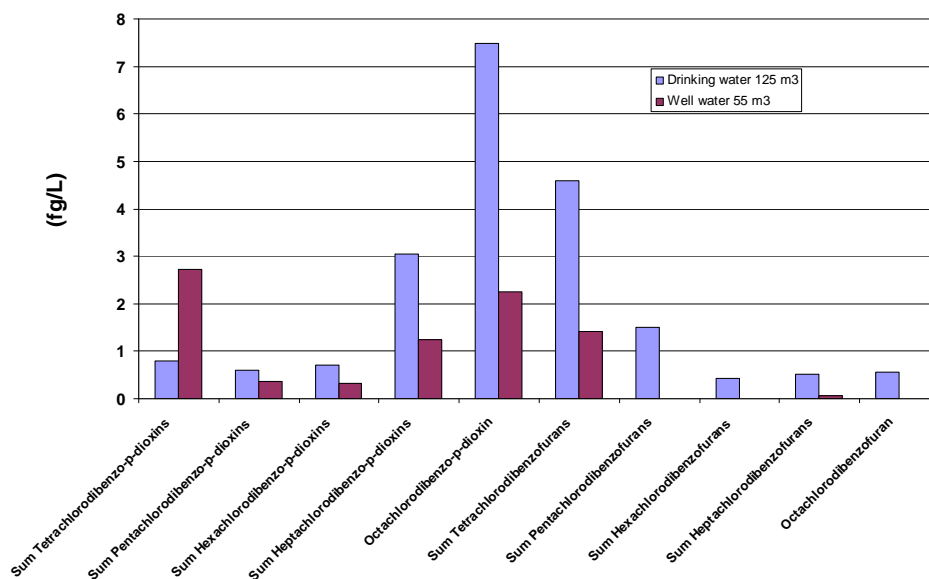


Figure 1: Pattern of the sum of PCDD/F of two different drinking water sources

Pattern of PCDD/F and sometimes also PCB have been recognized as source related fingerprints in case of emissions of different types of facilities, chemical impurities, and biota. For the two different waters a similar picture could be obtained since the pattern of PCDD/F and also PCB are different (Figures 1 and 2). For PCDD/F it is obvious that on one hand the compounds with higher water solubility are more pronounced, but also the OCDD and HpCDD is elevated again, possibly due to transport at nano-materials into the groundwater reservoirs as compartment of the two water sources.

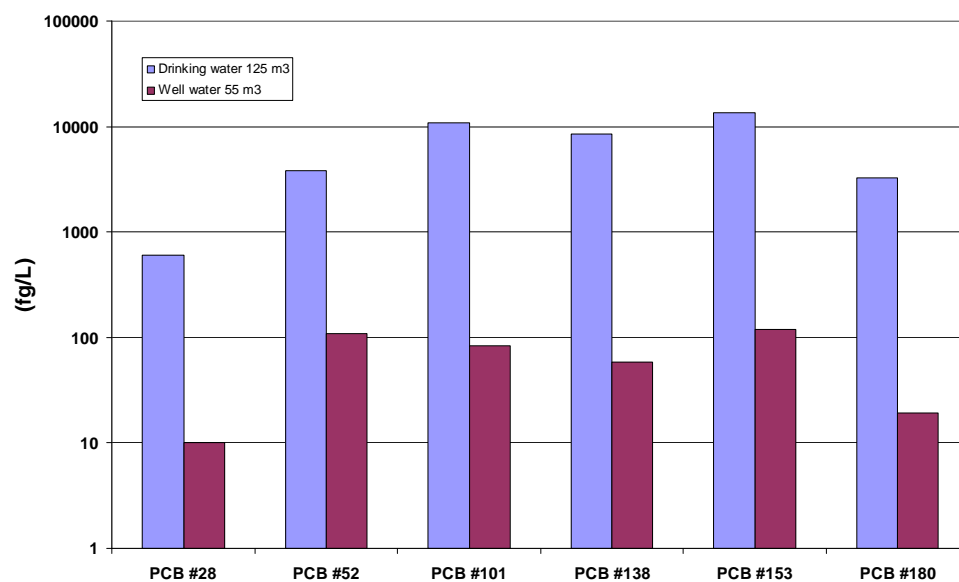


Figure 2: Pattern of the indicator PCB of two different drinking water sources

Also for PCB slight qualitative, but moreover a quantitative difference above a factor of 10 is visible. In conclusion it could be shown that persistent organic pollutants of low water solubility are present in

groundwater-related drinking water. The concentrations are far below a critical limit of intake for humans and the environmental biota, but indicative for the potential of those compounds with respect to ubiquity and persistence, even in drinking water. The qualitative and quantitative information gathered here and in further investigations seem to open the field of source attribution and fingerprinting.

References

1. WFD: Directive 2000/60/EC of the European Parliament and of the Council of 23 October 2000, OJL 327, 22 December 2000, pp. 1-73
2. El-Kady A. A., Abdel-Wahhab, M. A., Henkelmann B., Belal M. H., Morsi M. K. S., Galal S. M., Schramm K.-W. *Chemosphere* 2007; 68: 1660
3. Zielinski, M., Ligocka D., Wesolowski W. *Organohalogen Compounds* 2008; 70: 1698