

## CRITICAL ANALYTICAL ASPECTS TO DETECT PCDDs AND PCDFs IN THE VENICE LAGOON AT THE LOW LEVEL OF 13 fgTE/L

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### INTRODUCTION

The need to protect public health and the aquatic environment leads national and international agencies to establish quality standards for water pollutants. Risk assessment, evaluation of costs and benefits, and technological considerations induce the authorities to set limits as low as feasible to minimize the risk associated with exposure to toxic chemicals. However, in some cases, the limits are so low that the ensuing analytical task to verify their implementation becomes a serious problem. Such may be the case of the example we report upon here. The Decree (1) promulgated by the Italian Ministry of the Environment on April 23, 1998, concerning the "quality criteria for water and characteristics of depuration plants in the Venice lagoon" sets a quality standard for the PCDDs and PCDFs in the water phase at the value of 13 fgTE/L. This is very low analytical level to deal with, even lower than the maximum tolerable limit of 50 fgTE/L adopted by the Italian Advisory Toxicological Committee for the substances of interest in surface waters (2,3). Although a recent paper (4) has reported detection of PCDDs and PCDFs in Venice lagoon wastewater in the range of 20–31 fgTE/L, suggesting that the detection sensitivity target might be readily reached (at least in the special case where all congeners but one are undeterminable, their detection limits set to zero in calculations), we believe that the difficulties to carry out this type of assay still remain to be highlighted. This paper focuses on some of the numerous problems connected with the determination in water of such low levels of PCDDs and PCDFs.

### DISCUSSION

***Efficiency of sampling system.*** Götz and coworkers (5) showed that the PCDD and PCDF levels present in the aqueous phase are a few orders of magnitude lower than those found in the suspended particulate fraction, so that, in most cases, the determination of the particle-bound component is a good approximation of the total water load. However, the above mentioned Decree establishes standards only for the PCDD and PCDF fraction present in the water phase, whose collection implies the overcoming of remarkable technical difficulties. Difficulties in sampling are principally due to the very low concentrations of the dissolved substances due to both their high affinity toward the particulate matter and low solubility. Only few examples of sampling systems capable of separating the particulate matter from the dissolved fraction are reported in literature (5–8). The issue of their efficiency, especially when dealing with the dissolved fraction, is generally left unattended. When an environmental limit has been established, an official analytical method is required to monitor microcontamination concentration levels reliably. A validation process will verify the applicability of the method to the field for which it has been developed. Obviously, the higher is the efficiency of the sampling technique the more representative the samples are.

**The "blank" question.** In an analytical procedure of ubiquitous pollutants, the choice of a suitable blank becomes a very hard issue in particular when concentration levels are extremely low. The ideal blank is represented by the so-called reference matrices (9). They are virtually free from the analytes and contain potential interferences in the concentrations expected to be found in the samples to be analyzed. Reference waters simulating the sample matrix and, above all, not containing PCDDs and PCDFs in detectable amounts are not easily available, so they should be prepared. This may be done by passage through an extraction system that has been proven to perform a complete removal of the analytes from the matrix. This sampling system should then be used for the collection of both the sample and the blank matrix. The handling of liquid volumes in the order of one cubic meter is not simple. The practical difficulties of using such a blank matrix has led many laboratories to choose different solutions. The most practical, and practiced, is the use of a "reagent blank". However, especially when the analytical target has a very low concentration and the volume of the sample is large, the task to obtain a "clean" reagent blank, that is a blank whose contamination load is at least one order of magnitude lower than the target one, is very demanding. The elimination of all possible interferences is also essential and very efficient cleanup procedures have to be used.

**Number of samples.** In studies of pollutant distribution in the aquatic environment (water, sediments, and biota) a limited number of samples is often collected to characterize a large area. As known, in the definition of sampling strategy the establishment of the optimum number of samples is of great importance to guarantee the representativeness of the experimental data to be produced. This is even more important when the dissolved contaminants are present at such low levels as for PCDDs and PCDFs in water. Contamination in samples collected close to a pollution source may be some order of magnitude higher than those sampled in a relatively uncontaminated area. As an example of a petty and common contamination source in the Venice lagoon, we have calculated the release of PCDDs and PCDFs in sea waters caused by the death and subsequent decomposition of a marine organism. As previously reported (10), the PCDD and PCDF levels in Venice lagoon mussels grown in clean areas appear to be characterized by an average PCDD and PCDF level of 360 fgTE/g fw (CI 95%, 290–460 fgTE/g). Therefore, some 140 L of waters may be contaminated at level of 13 fgTE/L (the standard set for the Venice lagoon waters) after the death of a single 5-g mussel! On the same line, the decomposition of 100 g of a single mackerel (PCDDs and PCDFs were measured at levels of 590 fgTE/g) might pollute over 4500 liters, deeply affecting the results of a sample taken nearby (11). So, especially when the observance of a quality standard has to be controlled, it is highly recommended that statistically significant samples are taken in different locations.

**Examples of PCDD and PCDF determination in water.** In Table 1 some examples of PCDD and PCDF determination in water matrices are reported. Typical sample sizes range from 150 to 2000 L; analytes were measured at fgTE/L levels. The efficiency of sampling apparatuses has never been demonstrated. In some cases, the hydrophobic solid sorbents used on occasion for the collection of dissolved PCDDs and PCDFs were spiked with <sup>13</sup>C- or <sup>2</sup>H-labeled internal standards before sampling. This procedure may provide a proper correction for analyte losses during the sampling step, but does not give information about the efficiency of the collection system. Although information on blanks are generally not available, reagent blanks are run by some of the authors cited in the table. It is worth noticing that although the sampling apparatuses and the analytical methods described in the reviewed literature made use of sophisticated instrumentation, specifically designed and built for the purpose, and required good facilities, the analytical

problems discussed in this paper remained unresolved. However, in the research activities exemplified in Table 1, realistic hypotheses, such as the efficiency of the sampling system or the representativeness of a reagent blank instead of a reference blank matrix, can reasonably be assumed. When legal significance is to be associated to a result, the hypotheses should be experimentally demonstrated and made into sound experimental methods.

**Table 1. Examples of PCDD and PCDF determination in water matrices**

Ref.	Sample (Sample size)	Sampling technique	TEQs (LOD for 2,3,7,8-TCDD) <sup>d</sup>
(5)	River water (500–1000L)	Centrifugation; <sup>b</sup> sorption on PUF plugs <sup>c</sup>	73–41 ng/kg <sup>b</sup> ; 4.0–17 fg/L <sup>c</sup>
(7)	River water (150–250L)	Filtration; <sup>b</sup> sorption on PUF plugs <sup>c</sup>	77 fg/L <sup>d</sup> ; (24 fg/L) <sup>d</sup>
(8)	River water (431 L)	Filtration; <sup>b</sup> sorption on PUF plugs <sup>c</sup>	14 fg/L <sup>d</sup>
(8)	Drinking water (1500 L)	Filtration; <sup>b</sup> sorption on PUF plugs <sup>c</sup>	2.9 fg/L <sup>d</sup>
(12)	Sea water (2000 L)	Filtration through glass fiber filters; <sup>b</sup> sorption on XAD-2 <sup>c</sup>	92 fg/L <sup>d</sup> ; (5 fg/L) <sup>d</sup>
(6)	Sea water (2000 L)	Tangential flow filtration; <sup>b</sup> sorption on PUF plugs <sup>c</sup>	0.8–3.3 fg/L <sup>b</sup> ; (0.05–0.2 fg/L) <sup>b</sup> 0.4–3.6 fg/L <sup>c</sup> ; (0.2–1.9 fg/L) <sup>c</sup>

(a) Values rounded off to two figures. (b) Particulate matter. (c) Dissolved fraction. (d) Particulate matter and dissolved fraction.

## REFERENCES

1. Decreto del Ministero dell’Ambiente 23/4/1994, G.U. Serie Generale n. 140, 18/6/1998
2. Commissione Consultiva Tossicologica Nazionale, Istituto Superiore di Sanità, ISSN-0394-9311, Serie Relazioni 98/3
3. di Domenico A; Regul. Toxicol. Pharmacol. **1990**, 11, 8
4. Raccanelli S, Favotto M, Bonamin V and Gianoli C; PCDD/PCDF Analysis by HRGC/HRMS/MS/MS in industrial wastewaters. Comparison of data obtained utilizing different clean-up and analytical techniques. Presented as last minute communication P39 at the 18<sup>th</sup> Symposium on Halogenated Environmental Organic Pollutants, Stockholm, Sweden, 1998
5. Götz R, Enge P, Friesel P, Roch K, Kjeller LO, Kulp SE and Rappe C; Chemosphere **1994**, 28 (1), 63
6. Broman D, Näf C, Rolff C and Zebühr Y; Environ. Sci. Technol. **1991**, 25 (suppl 11), 1850
7. Rappe C, Kjeller LO and Anderssen R; Chemosphere **1989**, 19 (suppl 1-6), 13
8. Rappe C, Kjeller LO and Kulp SE; Organohalogen Compounds **1990**, 2, 207

9. USEPA Method 1613, Tetra- through Octa-Chlorinated Dioxins and Furans by Isotope Dilution HRGC/HRMS, October 1994
10. di Domenico A, Turrio Baldassarri L, Ziemacki G, De Felip E, Ferrari G, La Rocca C, Cardelli M, Cedolini G, Dalla Palma M, Grassi M, Roccabella V, Volpi F, Ferri F, Iacovella N, Rodriguez F, Volpi F, D'Agostino O, Sansoni R and Settimo G; *Organohalogen Compounds*, **1998**, 39, 199
11. S Bayarri, L Turrio Baldassarri, A di Domenico, N Iacovella, F Rodriguez. Toxic organic microcontaminants in edible marine species from Adriatic Sea. This congress
12. Matsumura T, Ito H, Yamamoto T and Morita M; *Organohalogen Compounds*, **1994**, 19, 109.