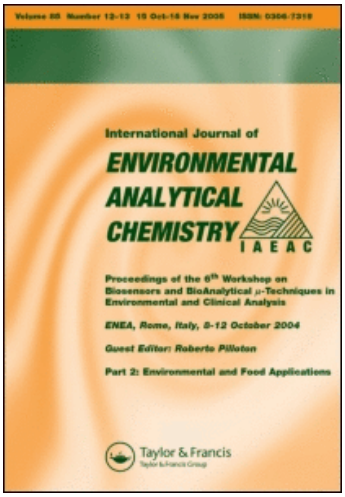

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Analysis of Polychlorodibenzo-p-Dioxins in Raw and Treated Waters. Part 1: Evaluation of Grab Sample Methodology for Part-per-Quadrillion Analysis

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ANALYSIS OF POLYCHLORODIBENZO-P-DIOXINS IN RAW AND TREATED WATERS. PART 1: EVALUATION OF GRAB SAMPLE METHODOLOGY FOR PART-PER-QUADRILLION ANALYSIS

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A liquid-liquid extraction and isolation procedure for the concentration of chlorinated dioxins from 12 L samples of treated and raw water was evaluated. It was demonstrated that water samples could be stored for one week prior to extraction without significant loss of dioxins. Extraction and isolation procedures were evaluated at pg/L levels by the use of ^{13}C labelled dioxin standards to determine recoveries. PCDD recoveries were quantitative (65–120%) except for octachlorodioxin where lower recoveries (40–60%) were due to losses in both the Florisil and carbopack column isolation steps. It is recommended that the concentration of each dioxin congener in water samples be calculated relative to the percent recovery of its specific ^{13}C congener.

KEY WORDS: PCDD, dioxin, liquid-liquid extraction, water analysis.

INTRODUCTION

Polychlorinated dibenzo-p-dioxins (PCDDs) occur primarily as by-products in the manufacture of other chemicals[1] and during incineration and combustion of municipal and chemical wastes.[2] They are ubiquitous in the environment and have been reported in fish,[3] animal[4] and human tissues.[5] It is possible, therefore, that these compounds may exist as pollutants in raw or treated water supplies. It is know that certain congeners, specifically 2,3,7,8-tetrachlorodibenzo-p-dioxin, can bioaccumulate and that they are toxic to most biological species[6] although there is a large variation in response. Therefore, to protect human health there is a need to detect PCDDs in drinking water at part-per-quadrillion levels.

In an aqueous medium organic pollutants of low polarity such as the PCDDs

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are traditionally analyzed by extraction with a water immiscible solvent followed by instrumental analysis.[7] Important factors in ultratrace analysis are initial sample size, procedures to isolate the pollutants from the matrix, and specificity and sensitivity of the detection system. The importance of these factors were emphasised during a study on the presence of PCDDs in the St. Clair River. A liquid-liquid extraction procedure was used and the extracts were prepared for GC/MS instrumental analysis using an isolation procedure previously developed for PCDD analysis in drinking water.[8] This particular protocol[10] specified small samples and a labour intensive manual extraction procedure. Substantial refinements were required in order to adapt this method to a practical and efficient monitoring methodology for PCDDs. Therefore, the objective of the present study was to determine which factors influenced recovery rates and precision and to devise an optimised protocol.

EXPERIMENTAL

Experimental Design

The following experiments were designed to allow identification of any low efficiency steps in recovery and thus provide an optimized procedure. In order to simplify the initial extraction, handling volumes were doubled. Evaluation of the behaviour of PCDDs in the Florisil and carbopack chromatography isolation steps was achieved by applying ^{13}C and ^{14}C tracers directly to the columns. To test linearity of recovery as a function of standard addition concentration, five different levels of ^{13}C-labelled tetra to octa chlorodioxin congeners ranging from 1 to 200 pg/L used. The effects of storage were tested by adding PCDD standard to water samples and storing for 0, 1 and 7 days.

Materials

Acetone, toluene, dichloromethane (DCM), pentane, methanol, hexane and cyclohexane were distilled-in-glass grade from Caledon Laboratories. DCM (GC capillary grade) and hexane (non-UV, distilled-in-glass) from Burdick and Jackson Laboratories were introduced during the study to consistently reduce background interferences. Purified water, glass wool and anhydrous sodium sulfate were prepared as described by LeBel *et al.*[9] The nitrogen was purified and scrubbed with Florisil. Florisil, PR grade from Supelco, Inc., was washed up to 10 times with DCM to remove interferences. The solvent was removed by nitrogen backflushing and the Florisil activated by heating at 300 °C overnight. It was then stored at 130 °C to maintain activation. The packing for the Carbopack column was prepared by thoroughly mixing 3.6 g of Carbopack C (80/100 mesh, Supelco Inc.) and 16.4 g of Celite 545. Standard addition solutions consisting of
^{13}C-1,2,3,4-tetrachlorodibenzo-p-dioxin(TCDD),
^{13}C-1,2,3,7,8-pentachlorodibenzo-dioxin(PnCDD),

^{13}C-1,2,3,6,7,8-hexachlorodibenzo-dioxin(HxCDD),
^{13}C-1,2,3,4,6,7,8-heptachlorodibenzo-dioxin(HpCDD),
^{13}C-octachlorodibenzo-dioxin(OCDD) and ^{14}C-2,3,7,8-TCDD, were obtained from Cambridge Isotope Laboratories, Woburn, MA. ^{14}C-OCDD was obtained from Pathfinder Lab Inc, St. Louis, MO. Stock solutions of each congener were prepared in toluene by transferring and diluting the contents of the received solution into appropriate volumetric flasks to obtain 5–10 ng/ul solutions. The final solutions for standard addition and quantitation purposes were prepared as required. An internal standard (IS) solution containing 50 pg/uL of pentachlorotoluene and octachloronaphthalene in toluene was prepared for GC/ECD quantitation. These compounds have retention times similar to those of the PCDD congeners without interfering with the detection of the target PCDD peaks.

Methods

Analytical Equipment Cleaning Procedures

To minimize interferences and contamination in order to attain very low detection limits ($\sim$1 pg/L), the state of cleanliness of analytical equipment was carefully controlled. Glassware was soaked in chromic acid for approximately 1 hour, rinsed thoroughly with distilled water followed by acetone, kept dust free by covering with solvent washed aluminum foil and finally rinsed three times each with toluene, acetone and DCM prior to use. The liquid-liquid extraction glassware was rinsed an additional two times with 100 mL of DCM and three times with pentane. Stirring bars were soaked in chromic acid for approximately 15 minutes, and rinsed with distilled water and acetone. Prior to use, they were sonicated for 1/2 hour in toluene and rinsed sequentially with acetone, DCM and pentane.

Water samples were collected in 4 L amber glass bottles (with Teflon-lined caps) that had previously held distilled-in-glass solvent and were then rinsed three times with acetone and allowed to dry before use.

The Pierce 0.1 mL conical reacti-vials used for storage of final extracts were cleaned by sequentially soaking and rinsing three times each with toluene, acetone and DCM. The Teflon lining of the Tuf-bond septa was washed three times with each of toluene, acetone and DCM.

Water Sampling Procedure

Twelve litre water samples were collected in three precleaned 4 L amber glass bottles. For raw and treated water samples, the tap was flushed for 5–10 minutes prior to sample collection.

Standard Addition Procedure

Standard addition was performed by injecting an appropriate volume ($<$10 uL) of

a standard solution of the various PCDD congeners, made up in toluene, into each sample bottle.

Liquid-liquid Extraction Procedure

The 12 L water samples were extracted in seven 1750 mL aliquots. Each aliquot was extracted three times with 200 mL portions of pentane, in a 2 L volumetric flask, by vigorous stirring with a Teflon-coated magnetic stirring bar for 20 minutes. After each extraction, the phases were separated using a 2 L separatory funnel, the aqueous phase returned to the volumetric flask for the next extraction and the pentane extract retained. After each aliquot had been extracted three times, the water phase was discarded. When all of the water sample had been extracted, the combined pentane extracts, concentrated as required to about 700 mL, was allowed to stand for approximately 1/2 hour to reduce any emulsion and any water was drained and discarded. The pentane extract was then concentrated to 3–5 mL by rotary evaporation and transferred to a 15 mL centrifuge tube with pentane rinsings. If an emulsion was present, the sample was centrifuged at 1600 rpm for approximately 10 minutes. The water layer was then removed using a Pasteur pipette and the remaining pentane concentrated to approximately 7 mL via nitrogen evaporation.

Isolation of Recovered PCDDs

The isolation method is similar to the one reported by LeBel *et al.*[8] Approximately 2 mLs of sulfuric acid was added to the pentane extract, the mixture vortexed and the acid layer removed. This step was repeated until the acid layer was clear. The pentane extract was then washed sequentially with purified water, potassium hydroxide and purified water once more. It was then dried by passage through a sodium sulfate column and concentrated by nitrogen evaporation to 0.5 mL in preparation for the Florisil and carbopack steps.

The Florisil and carbopack column cleanup steps were carried out as previously described[8] except that disposable 5 mL pipets fitted with glass wool plugs were used instead of chromaflex columns to avoid reuse of glassware. To remove interferences the pipets were rinsed with toluene, acetone and DCM, and dried using nitrogen evaporation prior to packing.

Gas Chromatography Determination

The extracts were analyzed by capillary GC/ECD on a Varian GC as described previously by LeBel *et al.*[8] For a typical analysis, the operating conditions were as follows: oven temperature: initial 80 °C, hold 1 minute, program at 15 °C/minute to 230 °C, hold 1 minute then program at 5 °C/minute to 290 °C, hold 4 minutes; helium carrier gas set at 2.0 mL/minute with nitrogen makeup gas set at 25 mL/

minute; detector at 325 °C; on-column injector program: 140 °C, then program at 100 °C/minute to 290 °C, hold time 25 minutes.

The PCDDs were quantified using an internal standard technique involving comparison of sample peak areas, normalized to the IS, with the corresponding normalized peak areas from an appropriate standard run under similar conditions. Pentachlorotoluene and octachloronaphthalene, which had been used previously for the determination of organochlorine pesticides, were used as internal standards. Recoveries were calculated using octachloronaphthalene as the primary internal standard because it eluted between HxCDD and HpCDD. However, if degradation of octachloronaphthalene due to GC conditions resulted in a variable response as determined by comparison of IS ratios, the recoveries of the PCDD congeners were recalculated based on pentachlorotoluene.

Gas Chromatography-Mass Spectrometry Analysis

Samples were analyzed as previously described[8] by GC-MS (VG-ZAB-2F) and by GC-tandem MS (TAGA 6000 MS/MS system).

Simplification Study

Twelve litre water samples of treated Ottawa tap water were distributed 3 L each in four 4 L sample bottles. Each bottle was extracted with 250 mL of pentane for 20 minutes by stirring with a Teflon-coated magnetic stirring bar placed in the sample bottle. The contents of the bottle were decanted into a separatory funnel and the aqueous layer returned to an empty sample bottle and extracted twice more. The pentane extracts were collected in a 1 L round bottom flask and evaporated to 5 mL on a rotary evaporator. The extract was then transferred to a 15 mL centrifuge tube and subjected to the usual isolation procedures.

Storage Study

Treated water samples, from a laboratory tap at the Environmental Health Centre of National Health and Welfare, and raw water samples, from a raw water tap at the Ottawa filtration plant laboratory on Lemieux Island, were collected in 4 L amber glass bottles. Twenty-seven bottles of each water type were fortified with the ^{13}C-PCDD standard addition mixture to give 50 pg/L of each congener. Nine non-fortified bottles of each water type were used as blank samples. Samples were allowed to reach room temperature prior to standard addition to ensure that all of the standard, which was made up in toluene, dissolved in the water. The volumes of toluene solution added (< 10 uL/4 L water) are well below toluene's solubility in water (0.05% at 25 °C).

Triplicate 12 L fortified samples and one blank sample of each water type were stored at room temperature and extracted with pentane after 0, 1 and 7 days. After

extraction and isolation the recovered materials were made up to a final volume of 25 uL in IS solution and analyzed by GC/ECD.

Recovery Testing at Various Levels for GC/ECD and GC/MS Analysis

Triplicate 12 L samples of Ottawa tap water were treated by standard addition with 10, 25 and 100 pg/L of ^{13}C-1,2,3,4-TCDD, and 20, 50, and 200 pg/L of each of ^{13}C-1,2,3,7,8-PnCDD, ^{13}C-1,2,3,6,7,8-HxCDD, ^{13}C-1,2,3,4,6,7,8-HpCDD and ^{13}C-OCDD. Quadruplicate 12 L samples were treated with 0, 1 and 5 pg/L of the above congeners.

The samples were extracted and the analytes isolated as described and made up to a final volume of 25 uL for GC/ECD analysis and 10 ul for GC/MS analysis.

Florisil Column Elution Profile

Separate solutions (0.5 mL) containing 5 ng of ^{14}C-OCDD and 1 ng of ^{14}C-2,3,7,8 TCDD, respectively, were prepared in duplicate. One solution (0.5 mL) was prepared containing 2.5 ng of each of the ^{13}C-PCDD congeners. The solutions were applied individually to the Florisil column.

(i) For the radioactive congeners, the 2% methylene chloride in hexane eluate (10 mL) was collected separately and the methylene chloride PCDD eluate was collected in six 3 mL aliquots. The fractions were evaporated just to dryness with a stream of nitrogen and transferred to clear scintillation vials using three 1 mL toluene rinses. Scintillation cocktail (Beckman Ready Solve MP Cocktail, 10 mL) was added and the ^{14}C isomers were counted using a Beckman 7500 Model liquid scintillation counter.

(ii) For the ^{13}C congeners 12 × 2 mL aliquots of DCM eluate were collected, evaporated to near dryness and transferred to 0.1 mL conical micro-vials with DCM. The fractions were evaporated just to dryness with a stream of nitrogen and made up to 50 ul with IS solution. The fractions were then analyzed by GC/ECD.

Carbopack Column Elution Profile

Duplicate samples of the ^{14}C congeners and one sample of the ^{13}C congeners were prepared as for the Florisil elution profile determination.

(i) For the radioactive congeners the usual carbopack procedure was followed but the eluates usually discarded were collected in 1 mL aliquots and the final toluene eluate was collected in eight 2 mL fractions. The eluates were evaporated just to dryness, transferred to scintillation vials using three 1 mL toluene rinses and counted as described in the Florisil profile determination.

(ii) For the ^{13}C congeners the 30 mL of toluene used for the final eluate was

Table 1 Percent recovery of ^{13}C-PCDD in raw and treated water[a] stored for 0, 1 and 7 days.

PCDD	*Day 0*		*Day 1*		*Day 7*	
	Treated	*Raw*	*Treated*	*Raw*	*Treated*	*Raw*
n	3	5	3	6	3	6
TCDD	71(2)[b]	73(10)	80(11)	61(9)	61(8)	71(16)
PnCDD	102(11)	84(7)	104(2)	79(14)	89(2)	75(4)
HxCDD	92(9)	91(11)	92(4)	83(14)	80(5)	73(11)
HpCDD	95(16)	76(11)	112(2)	80(24)	73(12)	61(11)
OCDD	34(16)	42(8)	32(1)	43(7)	31(4)	38(6)

n = number of replicates
[a]Mean % recovery, values in brackets are standard deviations.
[b]Fortification level 50 pg/L.

collected in fifteen 2 mL aliquots. The fractions were processed and analyzed as for the Florisil elution profile determination.

RESULTS

Storage Study

The results from this experiment are presented in Table 1. Treated water samples were analyzed in triplicate and raw water samples were analysed 5 or 6 times. The error limit defined by the standard deviation reflects mostly procedure errors since the reading errors were small in comparison to the observed deviation. The recoveries observed for the congeners in treated water samples ranged from 31 to 112%. Average recoveries for these congeners can be distributed into three categories; octa at 32%, tetra at 74%, and penta, hexa, and hepta at 93%. The recoveries observed for the congeners in raw water samples ranged from 38 to 91%, with octa exhibiting the lowest recovery at 41%, tetra at 68%, and penta, hexa and hepta at 78%.

These mean recovery values for each congener, found by the standard addition method, are assumed to be consistent with their expected recovery levels in each sample set so that comparisons can be made between the various days.

Recovery Study

All samples were done in triplicate except for the 200 pg/L level which was done in quadruplicate. Results from this study are presented in Table 2. The error limit defined by the standard deviation reflects mostly procedure errors since the reading errors were small in comparison to the observed deviation.

The recoveries observed for the congeners ranged from 44 to 123%, with octa exhibiting the lowest recovery and penta exhibiting the highest recovery. Again, the mean recovery values for each congener, found by the standard addition

Table 2 Percent recovery of various levels of ^{13}C-PCDD from treated water by pentane extraction

PCDD Congener		*% Recovery at various standard addition levels (pg/L)*				
		1 ZAB-2F[b]	*5 TAGA*[c]	*20*[a] *GC-EC*	*50*[a] *GC-EC*	*200*[a] *GC-EC*
TCDD	NQ[d]	96(12)[e]	86(19)	61(19)	87(15)	54(4)
PnCDD	NQ	123(40)	92(26)	99(8)	89(11)	69(5)
HxCDD	NQ	97(20)	98(36)	90(2)	87(12)	76(7)
HpCDD	NQ	93(25)	78(27)	85(12)	82(3)	69(8)
OCDD	NQ	60(10)	51(17)	49(11)	47(11)	44(5)

[a]TCDD values are 10, 25 and 100 pg/L.
[b]GC-MS (High Resolution).
[c]GC-MS-MS.
[d]Peaks detected but too weak to quantify.
[e]Mean % recovery, values in brackets are standard deviations.

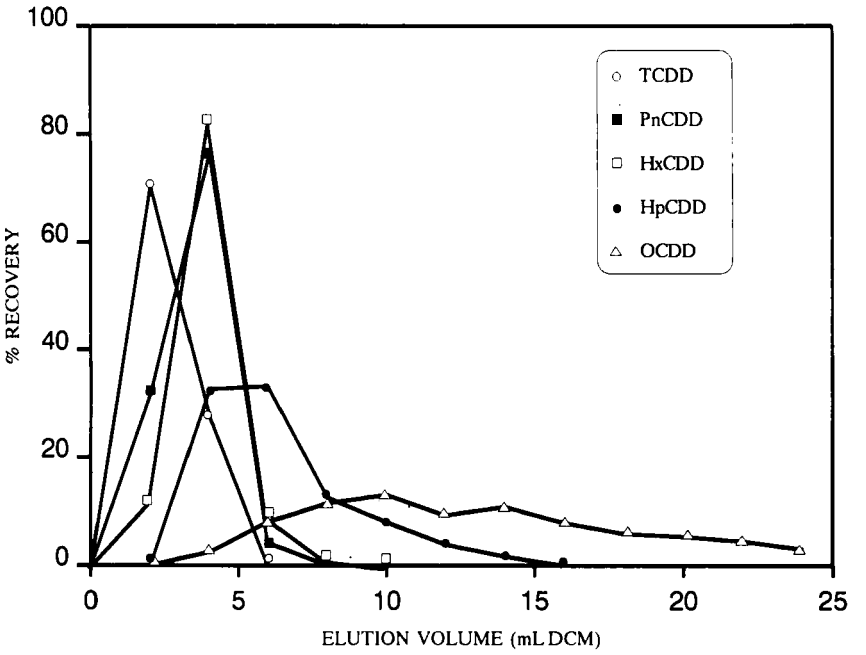

Figure 1 Elution profile using a Florisil column. % recovery of ^{13}C-PCDD's vs volume of DCM.

method, are assumed to be consistent with their expected recovery levels so that comparisons can be made between the various analyte levels.

Isolation Step Elution Profiles

The Florisil and carbopack elution profiles are shown in Figures 1 and 2. In the Florisil elution profile the first congener to completely elute from the Florisil column was TCDD, requiring 6 mL of DCM. PnCDD and HxCDD had similar elution profiles and cleared the column in about 10 mLs of DCM. HpCDD eluted

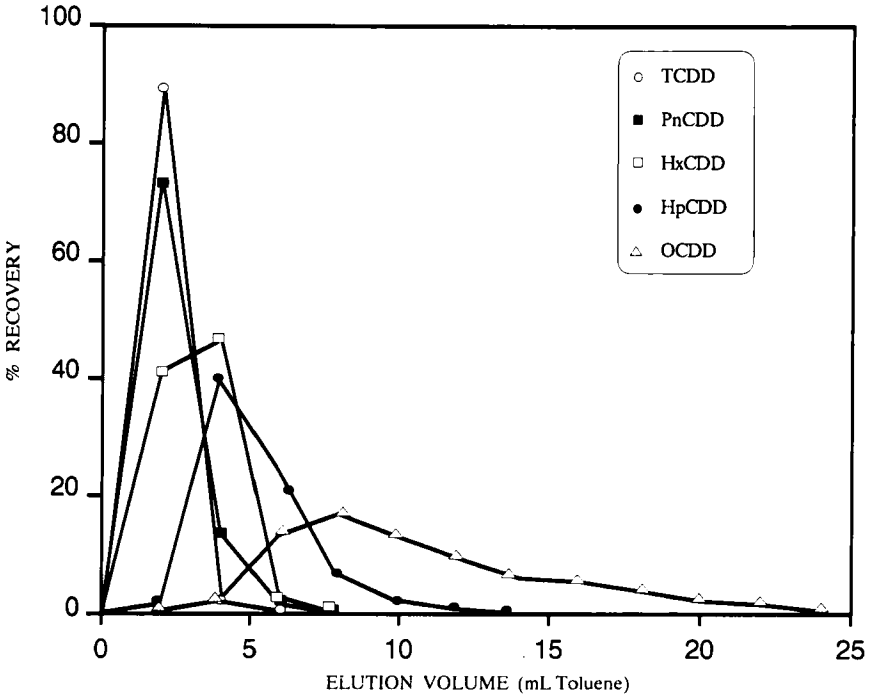

Figure 2 Elution profile using a Carbopack column. % recovery of ^{13}C-PCDD's vs volume of toluene.

more slowly and cleared the column in 15 mL DCM. The OCDD did not completely elute from the column after 24 mL of DCM.

In the carbopack elution profile TCDD and PnCDD were the first to elute. HxCDD was removed at 8 mL of toluene. HpCDD cleared the column in 12 mL of toluene. Some OCDD still remained on the column after 24 mL of toluene.

DISCUSSION

Liquid-liquid Extraction Procedure

As part of a study on the presence of PCDD/PCDF in St. Clair area drinking water sources, a protocol was suggested for the analysis of the water samples.[10] This protocol involved liquid-liquid extraction with pentane which required 15–18 hours per 12 L sample. The pentane extraction is labour intensive and there are many sample handling stages which can allow chemical contamination or procedure errors, giving rise to varying recoveries. A decision was made, therefore, to simplify and shorten the pentane extraction step by doubling the volume of aliquot extracted with a resultant time saving of 6 to 9 hours per sample. This modification was considered acceptable since the same ratio of organic solvent to water was maintained.

An attempt to simplify the method even further by performing the extraction directly in the sampling bottles using magnetic stirrers was not successful since experimental precision was adversely affected. The procedure did reduce the time

but problems were encountered because of inefficient stirring on the uneven bottoms of the sampling bottles.

Storage Study

The original protocol imposed a 48 hour limit on the storage of water samples before extraction and if the sample storage time exceeded this limit the sample had to be discarded.[10] This time limit cannot always be achieved because of transportation difficulties and laboratory scheduling. The recoveries of PCDD congeners for water samples stored at room temperature for up to 7 days indicate that the samples do not require analysis within 48 hours. Storage of samples for up to 1 week did not affect the recovery of spiked standards at the 50 pg/L level. The 50 pg/L level was used to allow easy analysis of the extracts by GC/ECD. A student's "t" test demonstrated that the mean values for day 0, 1 and 7 were not significantly different (95% confidence level). The need for storage studies for other water sources should be evaluated based on knowledge of the specific water source and local conditions.

Recovery Testing at Various Levels

In general, variance in PCDD recoveries tends to increase with decreasing concentration of contaminants. Recovery studies using water samples with standard addition levels of dioxin ranging from 1–200 pg/L were undertaken to test for interferences and to determine if recoveries varied as a result of analyte concentration. The % recoveries are within the expected ranges at all standard addition levels although the TCDD and OCDD congeners gave lower recoveries than the other isomers. Problems were encountered in GC/ECD analysis at lower standard addition levels because of background interferences, probably originating from the original DCM used which gave significant batch to batch variation when checked for ECD interferences. The isolation procedure was found to be adequate for evaluation purposes by GC/ECD for levels of these target compounds above 10 pg/L. For this reason only dioxin levels from 20–200 pg/L were analyzed by GC/ECD. The student's "t" test showed that there was no significant difference (95% confidence level) in recovery for the 20–200 pg/L range of all congeners.

PCDD levels from 0–5 pg/L were analyzed by GC/MS. No target compounds were detected in the blank or unfortified water samples. Samples fortified at the 1 pg/L level showed peaks for the ^{13}C-PCDD congeners but these were too weak to be quantified. The quantitation limits, therefore, lie between 1 and 5 pg/L.

Evaluation of Isolation Steps

Part of the quantitation and quality control process in the original protocol and the first phase of the study was based on the recovery of two labelled internal standards, ^{13}C-1234-TCDD and ^{13}C-OCDD, which were added to the water samples before extraction. Concentrations of native TCDD and PnCDD were

corrected based on the recovery of the ^{13}C-TCDD and those of HxCDD, HpCDD and OCDD were corrected based on the recovery of the ^{13}C-OCDD. As noted from recovery data from Tables 1 and 2, recovery of OCDD is usually considerably lower than other congener recoveries. Also, recovery of the TCDD congener is somewhat lower than penta to hepta congeners. Therefore correction factors based on TCDD or OCDD recoveries can lead to considerable errors in PnCDD, HxCDD and HpCDD concentrations.

In order to account for the differential loss in recovery of some congeners, the isolation steps were examined more closely since they were suspected as possible sources for analyte losses. Elution profiles were determined for the Florisil and carbopack column isolation procedures using the five ^{13}C-PCDD congeners. These profiles illustrate the strong retention of OCDD on both isolation columns. Other workers have also reported irreversible adsorption of OCDD to carbopack[11] and activated Florisil[12] adsorbents. The elution pattern of ^{14}C-2,3,7,8-TCDD was similar to the elution pattern of ^{13}C-1,2,3,4-TCDD and, therefore, justifies the use of 1,2,3,4-TCDD as a recovery surrogate. The lower recoveries of the tetra congeners could not be assigned to any specific steps in the extraction and isolation procedures.

CONCLUSION

Doubling handling volumes in the extraction step improves efficiency without loss of recovery. Water samples can be stored for up to 7 days without significant losses of dioxins. However, additional storage studies may need to be carried out on water sources of different quality.

Since the labelled TCDD and OCDD congeners in the protocol give reduced recoveries, these standards should not be used to correct for the recovery of other congeners. The ^{13}C-TCDD congener should only be used to correct for native TCDD and the ^{13}C-OCDD congener should be used only to correct for the native OCDD congener. Any of the labelled PnCDD, HxCDD or HpCDD congeners could be used to correct for either one of the native PnCDD, HxCDD or HpCDD congeners.

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References

1. E. H. Blair (ed.), *Chlorodioxins – Origin and Fate, Advances in Chemistry* (American Chemical Society, Washington, D.C., 1973), Ser. 120.
2. G. A. Eiceman, R. E. Clement and F. W. Karasek, *Anal. Chem.* **51,** 2343 (1979).
3. R. C. Dougherty, M. J. Whitaker, L. M. Smith D. L. Stalling and D. W. Huehl, *Environ. Health Perspect.* **36,** 103 (1980).

4. H. Heida, K. Olie and E. Prins, *Chemosphere* **15,** 1995 (1986).
5. J. S. Stanley, K. E. Boggess, J. Onstot and T. M. Sack, *Chemosphere* **15,** 1605 (1986).
6. O. Hutzinger, R. W. Frei, E. Merian and F. Pocchiari, *Chlorinated Dioxins and Related Compounds – Impact on the Environment* (Pergamon Press, Oxford, 1982).
7. B. K. Afghan, J. Carron, P. D. Goulden, J. Lawrence, D. Leger, F. Onuska, J. Sherry and R. Wilkinson, *Can. J. Chem.* **65,** 1086 (1987).
8. G. L. LeBel, D. T. Williams, J. J. Ryan and B. P.-Y. Lau, *Chlorinated Dioxins and Dibenzofurans in Perspective* (C. Rappe *et al.*, eds.) (Lewis Publishers, Michigan, 1986), pp. 329–341.
9. G. L. LeBel, D. T. Williams and F. M. Benoit, *J. Assoc. Off. Anal. Chem.* **64,** 991 (1981).
10. H. Tosine, R. Clement and R. Hunsinger, Methods for sampling and GC-MS analysis of drinking water for chlorinated dibenzo-p-dioxins and chlorinated dibenzofurans, Unpublished report.
11. S. Marklund, L.-O. Kjeller, M. Hansson, M. Tysklind, C. Rappe, C. Ryan, H. Collazo and R. Dougherty, *Chlorinated Dioxins and Dibenzofurans in Perspective* (C. Rappe *et al.*, eds.) (Lewis Publishers, Michigan, 1986), pp. 79–92.
12. R. J. Norstrom, M. Simon and M. J. Mulvihill, *Anal. Chem.* **23,** 267 (1986).