### The US EPA National Sewage Sludge Survey (NSSS) – a Recalculation

Christoffer Rappe and Lars Öberg Institute of Environmental Chemistry, Umeå University, S-901 87 Umeå, Sweden

#### Abstract

In 1988/89 US EPA conducted a survey (National Sewage Sludge Survey – NSSS) of 240 samples collected at 181 of the 15000 publicly owned sewage treatment works (POTW). We have used this database and calculated the concentrations of PCDDs and PCDFs expressed on dry weight basis to facilitate comparison between the NSSS and other studies. We have also calculated TEQ values for the PCDDs and PCDFs. The median value is 14 pg TEQ/g dry matter.

#### Introduction

In 1984 Lamparski *et al.* reported on the analyses of PCDDs and PCDFs in a dried sample of sewage sludge (biosolids) from Milwaukee, WI, USA, sold as fertilizer <sup>1)</sup>. Two samples were collected in 1983 and 1982, and the third sample was collected and sealed in 1933. In all three samples, the concentration of octaCDD was  $50\ 000 - 60\ 000\ pg/g$  dry matter (d.m.), and the concentration of heptaCDDs ranged between 7400 and 9700 pg/g d.m.

Weerasinghe *et al.* 1985 reported on the concentrations of PCDDs and PCDFs in two samples of sewage sludge from New York State, USA<sup>2)</sup>. One sample from Syracuse which represents an urban area with wood processing industries as well as many other industries, while the other sample should represent a rural area. The Syracuse sample contained 60 000 pg/g d.m. of octaCDD, while the concentration of this compound in the rural sample was 7600 pg/g d.m.

#### The NSSS study

Between July 1988 and March 1989 the United States Environmental Protection Agency (US EPA) conducted a survey of 240 samples collected at 181 of the totally 15 000 publiclyowned sewage treatment works (POTW) in USA. The samples were analyzed for several different organic and inorganic substances and are reported in & volumes covering approximately 6000 pages, the NSSS study. In 1993 the material became available on 14 diskettes. No summary or conclusion is given in this exclusive material <sup>31</sup>.

At DIOXIN '90 Telliard *et al.* published a paper where they discussed 211 of the 240 samples <sup>4)</sup>. However, for reasons given in the paper the data are presented on a "wet weight" basis that makes it very difficult to compare the NSSS-study with any other study where the data are presented on a dry weight basis. Moreover, the sum of the TEQ-values is not presented either in the original NSSS report or in the Telliard abstract <sup>3,4)</sup>. Here we report the concentration of 239 samples based on d.m., as well as the TEQ-concentrations found in the NSSS <sup>5)</sup>.

# LEVELS IN THE ENVIRONMENT

#### Table 1. NSSS data (concentration) for 2,3,7,8-substituted PCDD and PCDF congeners.

| Note: concentration in pg/g dry matter. Not TEQ.                               |
|--|
| 239 unique samples. Duplicates included. Non-detects excluded.                 |
| All data from DB-5 column. TCDF data from SP-2330 and DB-225 columns excluded. |

|                |         | C       | ration (p | og/g d.m.) |        |        | Mean            | Median |          |          |
|----------------|---------|---------|-----------|------------|--------|--------|-----------------|--------|----------|----------|
| Congener       |         | Max.    | Min.      | Mean       | Median | SD pop | No. obs. Occur. |        | contrib. | contrib. |
| TCDF           | 2378    | 310     | 0.19      | 20         | 9.6    | 36     | 151             | 63%    | 0.1%     | 0.2%     |
| PeCDF          | 12378   | 450     | 0.67      | 26         | 9      | 60     | 63              | 26%    | 0.1%     | 0.2%     |
|                | 23478   | 330     | 0.25      | 26         | 6.6    | 51     | 69              | 29%    | 0.1%     | 0.2%     |
| HxCDF          | 123478  | 2000    | 0.60      | 98         | 16     | 300    | 101             | 42%    | 0.5%     | 0.4%     |
|                | 123678  | 490     | 0.18      | 25         | 5      | 66     | 71              | 30%    | 0.1%     | 0.1%     |
|                | 234678  | 910     | 0.39      | 30         | 9      | 110    | 71              | 30%    | 0.2%     | 0.2%     |
|                | 123789  | 1300    | 0.25      | 78         | 11     | 200    | 41              | 17%    | 0.4%     | 0.3%     |
| HpCDF          | 1234678 | 9500    | 3.1       | 280        | 81     | 980    | 194             | 81%    | 1.4%     | 1.8%     |
| -              | 1234789 | 840     | 0.46      | 61         | 11     | 150    | 65              | 27%    | 0.3%     | 0.3%     |
| OCDF           |         | 95000   | 2.1       | 1300       | 210    | 7400   | 200             | 84%    | 6.5%     | 4.8%     |
| $\Sigma$ PCDFs | -       | 110000  | 7.0       | 1700       | 340    | 8200   | 208             | 87%    | 8.5%     | 7.9%     |
| TCDD           | 2378    | 120     | 0.33      | 11         | 2.7    | 23     | 44              | 18%    | 0.1%     | 0.1%     |
| PeCDD          | 12378   | 650     | 0.67      | 29         | 8.9    | 86     | 59              | 25%    | 0.1%     | 0.2%     |
| HxCDD          | 123478  | 870     | 0.72      | 40         | 9.7    | 120    | 61              | 26%    | 0.2%     | 0.2%     |
|                | 123678  | 1000    | 0.89      | 57         | 20     | 130    | 119             | 50%    | 0.3%     | 0.5%     |
|                | 123789  | 1300    | 0.26      | 58         | 21     | 150    | 96              | 40%    | 0.3%     | 0.5%     |
| HpCDD          | 1234678 | 70000   | 5.5       | 1300       | 420    | 5300   | 236             | 99%    | 6.5%     | 9.4%     |
| OCDD           |         | 1200000 | 44        | 17000      | 3600   | 88000  | 238             | 100%   | 83%      | 81%      |
| $\Sigma$ PCDDs |         | 1300000 | 15        | 18000      | 4000   | 93000  | 239             | 100%   | 92%      | 92%      |
| Total          |         | 1400000 | 33        | 19000      | 4200   | 100000 | 239             | 100%   | 100%     | 100%     |
|                |         |         |           |            |        |        |                 |        |          | _        |
| D/F ratio      |         | 150     | 0.8       | 20         | 15     | 19     | 208             | 87%    | 11       | 12       |

#### **Results and Discussion**

Table 1 contains the data for the 239 samples where the same analytical method was used and includes 2.3.7.8-substituted PCDDs and PCDFs: the maximum and the minimum concentrations as well as the mean and the median values. We also give the number and the frequency of a positive identification for the specific congeners.

OctaCDD was detected in 238 of the 239 samples (100%). On the other hand 1,2,3,7,8,9-hexaCDF was only detected in 41 of the 239 samples (17%). The three congeners with the highest TEF 2,3,7,8-tetraCDD, 1,2,3,7,8-pentaCDD and 2,3,4,7,8-pentaCDF were detected in 44 samples (18%), 59 samples (25%), and 69 samples (29%), respectively.

The highest concentration was found for the octaCDD in two samples from Billerica. MA. The reported values are 1 200 000 pg/g d.m. and 1 000 000 pg/g d.m. These samples also showed the highest concentrations of pentachlorophenol (PCP, 53  $\mu$ g/g) supporting a conclusion of a local source of both PCP and octaCDD, which is a known contaminant in technical PCP.

The highest concentration of 2.3,7,8-tetraCDD was found in the sample from Corinth. MS, 116 pg/g d.m. A sample collected in 1995 showed only 0.3 pg 2,3,7,8-tetraCDD/g d.m. with a major peak eluting very close to the 2.3,7,8-isomer indicating a false positive in the NSSS analyses <sup>60</sup>

### Dioxin '97, Indianapolis, Indiana, USA

#### Table 2. NSSS data (concentration) for PCDD and PCDF homologues, all congeners included.

| [              | 0       | Concen | tration ( | pg/g d.m |        |          | Mean   | Median   |          |
|----------------|---------|--------|-----------|----------|--------|----------|--------|----------|----------|
| Homologue      | Max.    | Min.   | Mean      | Median   | SD pop | No. obs. | Occur. | contrib. | contrib. |
| TCDFs          | 1000    | 0.5    | 62        | 16       | 150    | 159      | 67%    | 0.3%     | 0.3%     |
| PeCDFs         | 21000   | 1.6    | 260       | 35       | 1600   | 171      | 72%    | 1.2%     | 0.7%     |
| HxCDFs         | 6800    | 2.9    | 390       | 100      | 930    | 154      | 64%    | 1.7%     | 2.0%     |
| HpCDFs         | 44000   | 3.1    | 770       | 190      | 3600   | 199      | 83%    | 3.5%     | 3.8%     |
| OCDF           | 95000   | 2.1    | 1300      | 210      | 7400   | 200      | 84%    | 5.9%     | 4.2%     |
| Σ PCDFs        | 140000  | 8.2    | 2500      | 570      | 12000  | 210      | 88%    | 12%      | 12%      |
| TCDDs          | 1400    | 0.3    | 84        | 17       | 190    | 92       | 38%    | 0.4%     | 0.3%     |
| PeCDDs         | 2300    | 1.1    | 100       | 24       | 260    | 114      | 48%    | 0.5%     | 0.5%     |
| HxCDDs         | 5000    | 1.9    | 340       | 120      | 710    | 183      | 7.7%   | 1.5%     | 2.4%     |
| HpCDDs         | 110000  | 11     | 2300      | 780      | 8400   | 236      | 99%    | 10%      | 15%      |
| OCDD           | 1200000 | 44     | 17000     | 3600     | 88000  | 238      | 100%   | 75%      | 70%      |
| $\Sigma$ PCDDs | 1300000 | 30     | 19000     | 4400     | 97000  | 239      | 100%   | 88%      | 88%      |
| Total          | 1500000 | 52     | 21000     | 5000     | 110000 | 239      | 100%   | 100%     | 100%     |
|                | _       |        |           |          |        |          |        |          |          |
| D/F ratio      | 380     | 0.7    | 15        | 10       | 29     | 210      | 83%    | 8        | 8        |

Note: concentration in pg/g dry matter. Not TEQ.

Table 2 contains the same data based on congener groups *i.e.*, al. 38 tetraCDDs, all 14 pentaCDDs and all 4 heptaCDFs.

Table 3 shows the contribution to the toxic equivalents (TEQ) from each of the 2.3,7.8substituted congeners using the toxic equivalent factors (TEFs) accepted by WHO<sup>51</sup>. Based on means as well as medians the contribution of the PCDDs is 69% and by PCDFs 31%. The largest contribution comes from 1,2,3,7.8-pentCDD and octaCDD (13–14%) followed by 2,3,4,7,8pentaCDF and 1,2,3,4,6,7,8-heptaCDD (11%) and 2,3,7,8-tetraCDD (10%).

Table 3 also contains the mean and the median TEQ-values for the 239 samples analyzed. In a situation where two high outliers will have significant influence to the mean values (the two Billerica samples) the situation is much better expressed by the median value. The median value for the 1988/89 sampling of the 181 POTWs in the US is 14 pg TEQ/g d.m.

Several studies indicate a significant and dramatic decrease in the contamination of PCDDs in most environmental samples including human tissue. Sewage sludge samples from Switzerland and Sweden also shows a dramatic decrease during the period 1989 up to present time<sup>7)</sup>. The median value presented here from the 1988/89 sampling campaign in the US is probably at the higher end.

See other comments in Table 1.

## LEVELS IN THE ENVIRONMENT

#### Table 3. NSSS data (TEQ-values) for 2,3,7,8-substituted PCDD and PCDF congeners.

Note: concentration in pg TEQ/g dry matter.

See other comments in Table 1.

|           |         | Concentration (pg TEQ/g d.m.) |        |      |        |        | <u> </u> |        | Mean  | Median |
|-----------|---------|-------------------------------|--------|------|--------|--------|----------|--------|-------|--------|
| Congener  |         | Max.                          | Min.   | Mean | Median | SD pop | No. obs. | Occur. | TEQ % | TEQ %  |
| TCDF      | 2378    | 31                            | 0.019  | 2.0  | 1.0    | 3.6    | 151      | 63%    | 1.7%  | 3.2%   |
| PeCDF     | 12378   | 23                            | 0.034  | 1.3  | 0.44   | 3.0    | 65       | 27%    | 1.1%  | 1.5%   |
|           | 23478   | 170                           | 0.13   | 13   | 3.3    | 26     | 71       | 30%    | 11%   | 11%    |
| HxCDF     | 123478  | 200                           | 0.060  | 10   | 1.6    | 29     | 103      | 43%    | 8.4%  | 5.3%   |
|           | 123678  | 49                            | 0.018  | 2.6  | 0.54   | 6.7    | 72       | 30%    | 2.3%  | 1.8%   |
|           | 234678  | 91                            | 0.039  | 3.1  | 0.90   | 11     | 72       | 30%    | 2.7%  | 3.0%   |
|           | 123789  | 130                           | 0.025  | 7.9  | 1.4    | 20     | 42       | 18%    | 6.8%  | 4.7%   |
| HpCDF     | 1234678 | 95                            | 0.031  | 2.8  | 0.81   | 10     | 194      | 81%    | 2.4%  | 2.7%   |
|           | 1234789 | 8.4                           | 0.0046 | 0.6  | 0.11   | 1.5    | 67       | 28%    | 0.5%  | 0.4%   |
| OCDF      |         | 95                            | 0.0021 | 1.3  | 0.21   | 7.4    | 200      | 84%    | 1.1%  | 0.7%   |
| Σ PCDFs   |         | 630                           | 0.051  | 18   | 3.1    | 59     | 208      | 87%    | 31%   | 23%    |
| TCDD      | 2378    | 120                           | 0.33   | 11   | 2.7    | 23     | 44       | 18%    | 10%   | 9%     |
| PeCDD     | 12378   | 330                           | 0.34   | 15   | 4.5    | 43     | 61       | 26%    | 13%   | 15%    |
| HxCDD     | 123478  | 87                            | 0 072  | 4.2  | 1.0    | 12     | 62       | 26%    | 3.6%  | 3.4%   |
|           | 123678  | 100                           | 0.089  | 5.8  | 2.0    | 12     | 120      | 50%    | 5.0%  | 6.6%   |
|           | 123789  | 130                           | 0.026  | 5.8  | 2.1    | 15     | 96       | 40%    | 5.0%  | 6.8%   |
| HpCDD     | 1234678 | 700                           | 0.055  | 13   | 4.2    | 53     | 236      | 99%    | 11%   | 14%    |
| OCDD      |         | 1200                          | 0.044  | 17   | 3.6    | 88     | 238      | 100%   | 14%   | 12%    |
| Σ PCDDs   |         | 2000                          | 0.099  | 41   | 10     | 160    | 239      | 100%   | 69%   | 77%    |
| Total     |         | 2300                          | 0.23   | 57   | 14     | 200    | 239      | 100%   | 100%  | 100%   |
|           |         |                               |        |      |        |        |          |        | ····· |        |
| D/F ratio |         | 260                           | 0.073  | 7.7  | 3.8    | 19     | 210      | 87%    | 2.2   | 3.3    |

#### Literature Cited

- (1) Lamparski, L. L.; Nestrick, T. J.; Stenger, V. A. Presence of chlorodibenzo-p-dioxins in a sealed 1933 sample of dried municipal sewage sludge. *Chemosphere* **1984**, 13, 361-365.
- (2) Weerasinghe, N. C. A.; Gross, M. L.; Lisk, D. J. Polychlorinated dibenzodioxins and polychlorinated dibenzofurans in sewage sludges. *Chemosphere* **1985**, 14, 557-564.
- (3) US EPA, National Sewage Sludge Survey (NSSS) 1988. *NTIS* PB93-500403, PB93-111607, PB93-111615, PB90-107509, PB90-107491: **1989** and **1993**; pp. 1-6000.
- (4) Telliard, W. A.; McCarty, H. B.; King, J. R.; Hoffman, J. B. USEPA National Sewage Sludge survey results for polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans. Organohalogen Compd. 1990, 2, 307-310.
- (5) Ahlborg, U. G.; Becking, G. C.; Birnbaum, L. S.; Brouwer, A.; Derks, H. J. G. M.; Fceley, M.; Golor, G.; Hanberg, A.; Larsen, J. C.; Liem, A. K. D.; Safe, S. H.; Schlatter, C.: Waern, F.; Younes, M.; Yrjänheikki, E. J. Toxic Equivalency Factors for Dioxin-Like PCBs -Report on a WHO-ECEH and IPCS Consultation. December 1993. *Chemosphere* 1994. 28. 1049-1067.
- (6) Rappe, C.; Andersson, R.; Bonner, M.; Cooper, K.; Fiedler, H.; Howell, F. PCDDs and PCDFs in Mississippi sewage sludge and effluent from POTW in the state of Mississippi. 1997 (Manuscript in preparation).
- (7) Rappe, C.; Andersson, R.; Studer, C.; Karlaganis, G. Decrease in the concentrations of PCDDs and PCDFs in sewage sludge from Switzerland. **1997** (Submitted to DIOXIN '97).