

## PCDD CONTAMINATION IN A TRICHLOROPHENOL-PRODUCING PLANT

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### INTRODUCTION

The production of chlorinated phenols started in Spolana Chemical Company in 1965. Mainly the sodium salt of 2,4,5-trichlorophenoxy acetic acid, sodium pentachlorophenate, pentachlorophenol and 2,4,5-trichlorophenol had been produced. These products have had important uses as herbicides and pesticides (mainly for wood protection).

After a short time many workers got dermal lesions (chloracne), therefore the production of chlorophenols was stopped immediately and in 1968 the facility was closed. Because toxicological knowledge was lacking, it was not possible to precisely determine, what was the cause of the illness. At the beginning of the Seventies it was found and analytically determined that during the production of products mentioned above a group of very toxic polychlorinated dibenzo-p-dioxins and dibenzofurans have been formed, of which 2,3,7,8-TCDD was the most toxic isomer.

The main task was to provide a clear and exact picture of TCDD contamination around the facility and over the affected territory and to assess TCDD persistence in soil. Chemical wastes consisting mainly of chlorobenzene and by-products of trichlorophenoxyacetic acid have been dumped in steel drums distributed in the contaminated area.

Although several methods have been reported for the determination of trace amounts of TCDD in soil samples with the great amounts of co-extracted materials (1-7), no method was suitable for our purpose. We have developed and used a new analytical method for our type of soil samples.

### EXPERIMENTAL

#### Extraction:

Soil samples were weighed (50 g) as received and spiked with 1-10 ng of the internal standard,  $^{13}\text{C}$ -2,3,7,8-TCDD, and extracted with three successive portions (70, 30, 20 ml) of mixtures 3:1 in volumes of hexane-acetone. After sedimentation, each fraction was filtered through paper into a separating funnel.

Aqueous samples (10 g) were mixed with 30 ml methanol, 30 ml water and 5 ml 5M-KOH and the mixture was extracted with three successive portions of hexane. Extracts thus obtained were collected together in a separator-funnel and washed with 5 ml 5M-KOH and with water. The organic phase was then evaporated in a rotary evaporator.

#### Clean-up:

Extracts from soil samples were successively treated by shaking with 5M-KOH, water, concentrated sulfuric acid and water. The resulting organic phase, usually colorless, was filtered through a filter funnel containing anhydrous sodium sulfate and concentrated in a rotary evaporator to approximately 1 ml.

Extracts from soil and aqueous samples were then purified on a multi-layer column. The glass column (250x10 mm I.D.) was packed (from bottom to top) with a glass-wool plug, activated silica gel 100/250 (0.5 g), 10% silver nitrate-impregnated silica gel (1.5 g), 33% (w/w) sodium hydroxide-impregnated silica gel (1.5 g), activated silica gel 100/250 (0.5 g), 44% (w/w) sulfuric acid-impregnated silica gel (4 g), activated silica gel (1 g) and finally anhydrous sodium sulfate (2 g). Prior to the application of the sample, the column was rinsed with 30 ml hexane. The eluate was concentrated to dryness on a rotary evaporator.

The last step was the isolation of TCDD isomers and the separation of 2,3,7,8-TCDD from other TCDD isomers. This step was performed on a column filled with aluminium oxide. Macrocolumn (150x10 mm I.D.) was filled with glass-wool plug, ICN Alumina B Super I (5 g) and anhydrous sodium sulfate (2 g). The residue was applied with minimal volumes of hexane. The column was then eluted sequentially with 75 ml hexane/methylene chloride (98:2), 35 ml hexane/methylene chloride (80:20) and finally with 25 ml methylene chloride. The third fraction containing 2,3,7,8-TCDD was collected and concentrated. The residue from the macrocolumn was then transferred with hexane onto the microcolumn (150x4 mm I.D.) filled with glass-wool plug on bottom and then with ICN Alumina B Super I (1 g) and anhydrous sodium sulfate (1 g). The column was then eluted sequentially with 15 ml hexane/methylene chloride (98:2), 7 ml hexane/methylene chloride (80:20) and 5 ml methylene chloride. The third fraction was collected and evaporated to dryness on a rotary evaporator. The residue was quantitatively transferred using benzene to a Reacti-Vial (Pierce) and evaporated, using a stream of prepurified nitrogen, to dryness.

#### GC/MS analysis:

High resolution gas chromatography with mass selective detection was done with HP 5970B-MSD. SIM data were acquired for the following selected characteristic ions:  $m/e$  332 and 334 (internal standard  $^{13}\text{C}$ -2,3,7,8-TCDD). The gas chromatographic separations were performed using SP-2331 (60m x 0.32mm, 0.2  $\mu\text{m}$  film thickness, Supelco) column with a temperature program starting at 200°C isothermal for 1 min followed by programming to 240°C/min. The samples were dissolved in toluene and injected in the splitless mode. Split/splitless injector was held at 260°C. Helium was used as carrier gas.

## RESULTS

In 1975 the first 23 samples of wastes have been collected and analysed in order to determine a content of PCDDs. Samples were analysed by comparative gas chromatography and all findings were in the range of 0.6-6.555  $\mu\text{g}$  of PCDD/g of a sample. Due to the poor sensitivity capabilities of the used available analytical method, the results were not precise. In 1982 the improved and advanced GC/MS method with capillary columns was used to evaluate the waste samples mentioned above. The values of 2,3,7,8-TCDD were within the range of 0.6-2.0  $\text{ng g}^{-1}$  (part per billion). Recent findings (1989) showed the same values. About 600 drums (200 liter) containing different waste liquids are deposited in the contaminated area. This fact causes a potential danger of leaching-out of the drums and contamination of groundwater, even the drums are sufficiently isolated. Groundwater have been sampled from four sites placed regularly around the contaminated area. Amounts of 2,3,7,8-TCDD in these waters have not been changing during past 8 years and reached maximally up 0.005  $\mu\text{g/L}$ .

In 1986 more than one hundred soil samples were collected from the periphery of the plant (at the distance of 5-15 meters from the building). Samples were analysed for 2,3,7,8-TCDD by standard procedures based on a sorbent extraction, impurities removal, silica gel/alumina cleanup and HRGC/LRMS determination. The recovery was in the range of 44 to 112% with a medium value of 55%. The detection limit was 10 ppt at signal-to-noise ratio S/N 2.5.

Level of 2,3,7,8-TCDD in the soil samples collected from a depth of 20 cm ranged from 0 to 29.8  $\text{ng g}^{-1}$  (0-6.0  $\text{mg m}^{-2}$ ) and in the samples from a depth of 20 to 50 cm, the levels ranged from 0 to 0.07  $\text{ng g}^{-1}$  (0-0.011  $\text{mg m}^{-2}$ ).

To compare the level of contamination, we had to determine 2,3,7,8-TCDD in several samples from "non-contaminated" areas in the City of Neratovice. 2,3,7,8-TCDD levels in these samples have been within 0-0.1  $\text{ng g}^{-1}$  2,3,7,8-TCDD. Results have been taken as a background.

Samples of soil collected at a distance of 50-80 meters from the plant contained from 0-0.06  $\text{ng g}^{-1}$  2,3,7,8-TCDD. These values are essentially background levels.

It is shown that higher amounts of 2,3,7,8-TCDD in soils are only in the immediate vicinity of the now defuncted plant. The monitoring of the PCDD contaminated around the plant is still continuing and obtained results present important bases for the preparation of a large remedial action concerning TCP-production plant.