PCDF/PCDD LEVELS IN SEDIMENT PROFILES FROM A NORWEGIAN FJORD CONTAMINATED BY EFFLUENTS FROM A NICKEL REFINERY

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INTRODUCTION

Polychlorinated dibenzofurans (PCDF) and to a lesser extent dibenzo-p-dioxins (PCDD) are formed in the production process of a nickel refinery plant at Kristiansand, South-Norway [1]. The present technique involves dissolution of a Ni-Cu converter mat by chlorine leaching, precipitation processes employing Cl_2 for removal of metals such as Pb, and liquid/liquid extraction of Co from a Ni-Co solution using trioctylamine and alkylbenzenes as solvent. The latter is also the main carbon source. Electrolysis of $NiCl_2$ and $CoCl_2$ as well as removal of noble metals are further steps. Chlorine is recirculated and cleaned by a scrubber system. PCDF/PCDD was found in the waste waters from the different processes [1]. Since the applied temperatures normally do not exceed 150-200 °C, they are probably formed mainly by catalytic effects.

Until 1983/84 another process was used to convert $NiCl_2$ to NiO for about 17 years. $NICl_2$ cristals were blown into a fluidized bed reactor and converted by adding air and propane to NiO, HCl and traces of Cl_2 at about 800 °C. The flue gases were washed by a sea water scrubber and the waste water emitted directly to the fjord (see map in Figure 1). The TCDF pattern in the pipe residues of this technique contained only 1,2,7,8- and 2,3,7,8-TCDF [1]. The TCDF profile in a single sediment core taken at K18 in 1987 was also dominated by these isomers and in addition 1,3,7,8/1,3,7,9-TCDF. The present effluents, however, show a different TCDF-distribution (see Figure 1). A preliminary conclusion was therefore that the old conversion process was the main

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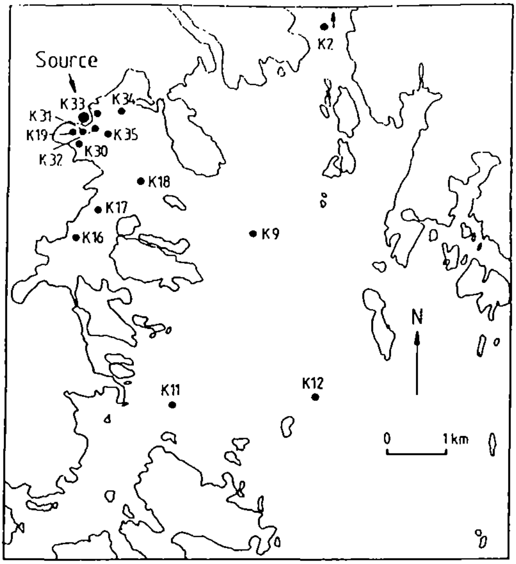

Figure 1: Sediment sampling sites in the Kristiansandsfjord, Norway (8° E, 58° 10′ N). K2 is situated about 3 km more north than indicated.

source of the PCDF/PCDD levels found in the sediments. This was further supported by the high level of 1.8 ppb 2,3,7,8-TEQ (Nordic model) in the sediment sample compared to the present annual emission of 2-4 g 2,3,7,8-TEQ by the remaining waste water effluents.

EXPERIMENTAL

Sediment samples (top layer 0-2 cm) from 14 sites (see Figure 1) were collected in 1988 using a Niemistö gravity corer [2]. The cores were sectioned in 2 cm intervals. A modification of the analytical procedure described in [3] was employed.

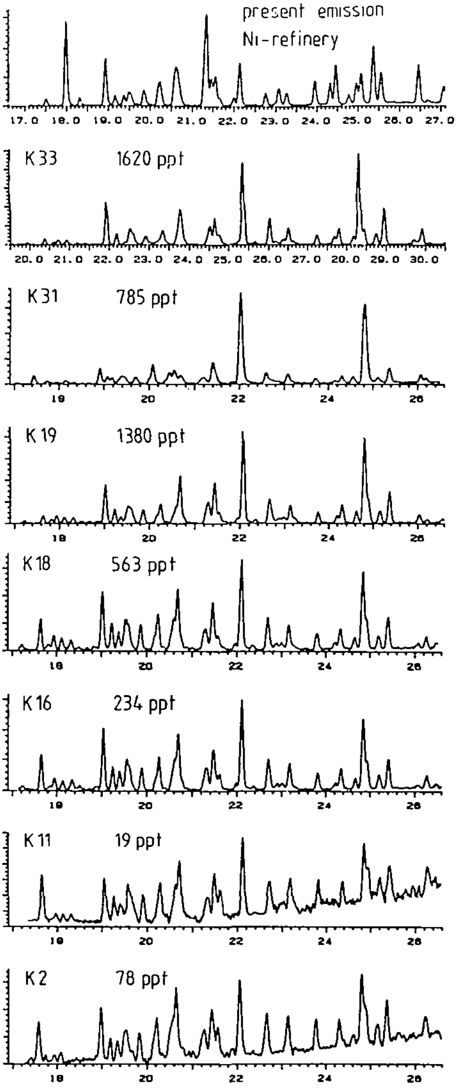

Figure 2: Tetrachlorodibenzofuran mass fragmentograms of the present waste water emission and selected sediment samples (top layer, 0-2 cm). Concentrations are given as ppt 2,3,7,8-TEQ. The levels in the not shown samples were: K35: 1256; K30: 704; K17: 661; K12: 94 and K9: 49.5.

RESULTS AND DISCUSSION

The TCDF isomer pattern of the 0-2 cm top layers is different from that of the present waste water emissions (see Figure 2). Close to the source (K19-K35) the profiles are clearly dominated by 1,2,7,8- and 2,3,7,8-TCDF. Farther away at K16-18, the TCDF isomer pattern is still dominated by these two isomers. Stations K9, K11 and K12 show profiles that resemble more and more that of K2 which is not influenced by the source. The PCDF/PCDD levels expressed as 2,3,7,8-TEQ follow in general these changes starting at levels over 1 ppb close to the factory and ending well below 100 ppt at the stations K9, K11 and K12.

A profile analysis of the horizons at K35 showed for the 0-2, 4-6, 8-10 and 12-14 cm levels gave a very similar profile as that of K33 (Figure 2). Beside the dominating 1,2,7,8- and 2,3,7,8-TCDF also minor amounts of other isomers were present. However, at 16-18 and 22-24 cm an isomer pattern was found which was identical with the profile from the pipe residues of the old process. This consisted only of the two main TCDF-isomers. The 2,3,7,8-TEQ levels decreased from 1250 ppt (0-2cm) via 690 ppt (4-6 cm) to 570 ppt (8-10 cm). Then, however, the concentrations increased to 1390 ppt (12-14 cm) and declined again to about 400-450 ppt (16-18 and 22-24 cm). A similar change from 1380 ppt (0-2 cm) via 4150 ppt (4-6cm) and 994 ppt (8-10 cm) to 2850 ppt (20-22cm) was found at site K19. Whether these variations are caused by changes in the emissions due to the old procedure or by mixing processes in the sediments is yet not known. At the stations K17 and K18 a continuous decrease from 500-600 ppt (0-2cm) to 40-50 ppt (8-10 cm) was observed.

The changes in the PeCDF isomer profiles were less significant but confirmed the findings from the analysis of the TCDF profiles. The HxCDF isomer distributions were nearly identical for all samples. Also the PCDD isomer patterns did not contain any source specific information.

Based on these results our present conclusion is that the former $NiCl_2/NiO$ conversion process is mainly responsible for the observed PCDF/PCDD levels in the fjord sediments.

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