DIOXINS AND ORGANIC POLLUTANTS IN DANISH SEWAGE SLUDGE AND HARBOUR SLUDGE

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Introduction

In the middle of the previous decade dioxin emission from incineration had been better studied than all other sources. Much lesser was known about the emission of PCDD/F to the aquatic environment than to the atmosphere. Since the discovery of dioxins in sewage sludge[1], this source has been recognised as a route for introduction PCDD/F into the food chain, potentially exposing humans as well as domestic animals and wildlife. In Denmark all wastewater is cleaned in municipal or industrial wastewater treatment plants, making the country a model for the investigation of PCDD/F in sewage sludge. It was the primary aim of the present project to estimate the level and geographical distribution of PCDD/F in sewage sludge. Furthermore, a range of classic environmental pollutants was analysed to evaluate the correlation between dioxins and other contaminants - in particular chlorinated ones. To evaluate the pollution of the marine environment, also harbour sludge was investigated. In an effort to identify all sources, the EU commission sponsored an investigation of dioxins from industrial sources other than waste incineration. The present investigation was initiated as a sub project under this program.

Methods and materials

The sewage sludge was produced in Danish wastewater treatment plants (WWTPs), 28 samples from rural, 10 from provincial and 5 from urban regions. The samples were taken in co-operation with local authorities. The harbours covered 5 samples from small and 4 from large harbours kindly donated by NERI Department of Marine Ecology. Samples stored at -20°C until analysed.

The substances analysed comprised PCDD/F and pollutants selected from the classes PAH, chlorobenzenes, chlorophenols, nonylphenol, phthalates, chlorophenoxy acids and PCB.

PCDD/F analysis: Air-dried sample spiked with 10 ^{13}C-labelled PCDD/F, Soxhlet extracted in toluene. Cleanup on silica gel / NaOH, silica gel / H_2SO_4, acidic Al_2O_3, Supelco Carbopack C/Celite. Analysis by GC/MS at resolution 10 000.

Analysis of selected pollutants[2]: Extraction in acetone n-hexane 1/3, extract washed with dilute NaOH and HCl, organic phase from acidic wash methylated with diazomethane. Combined extract analysed by CG/MS at resolution 10 000.

Results and discussion

Fig. 1 shows results for sewage sludge ranging from 1.4 - 51 ng/kg dm WHO-TEQ with mean and standard deviation (sd) 9.2 and 10.5 ng/kg dm WHO-TEQ, respectively. All the values below the mean are from rural plants. Comparable levels are reported for American[3] and Swedish[4], higher for Spanish sludge [5].

Fig. 2 shows results for harbour sludge the ranging from 0.2 – 47 ng/kg dm with mean and sd 17 and 20 ng/kg dm WHO-TEQ, respectively, about the double of that for sewage sludge. A discontinuous jump is seen between small and large harbours.

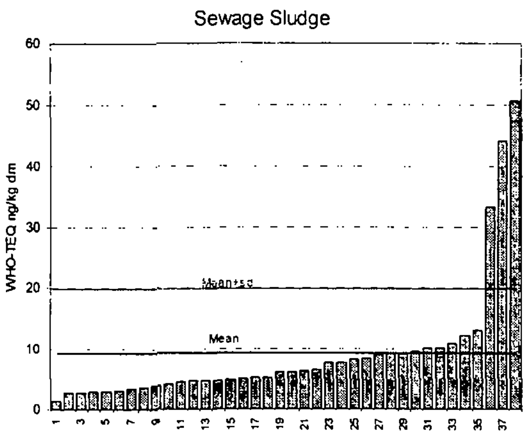

Fig. 1

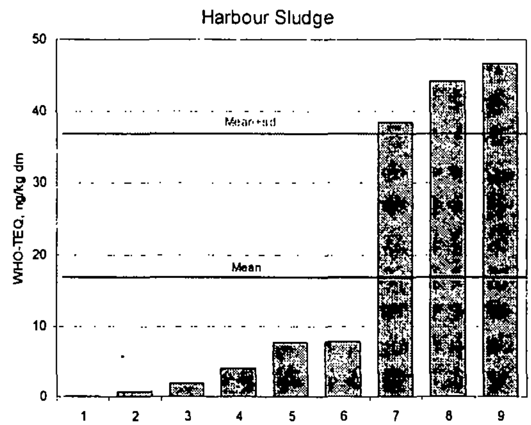

Fig. 2

Fig. 3 shows the TEQ contribution from each congener in sewage and harbour sludge, mean of all samples. The maximal TEQ contributor is 2,3,4,7,8-PeCDF for sewage and harbour sludge. The main PCDD contributors are 1,2,3,4,6,7,8-HpCDD for sewage sludge and 1,2,3,6,7,8-PeCDD for harbour sludge. Harbour sludge has much higher 1,2,3,4,7,8,9-HpCDF. The similarities and differences suggest common as well as different sources.

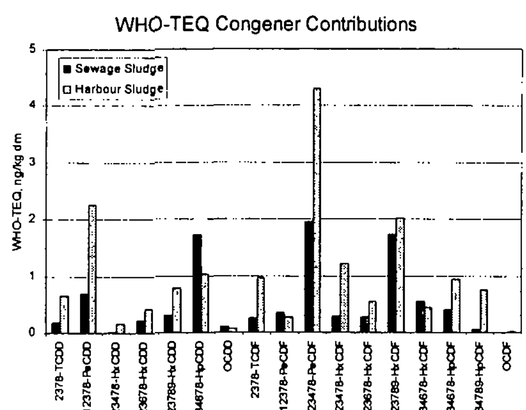

Fig. 3

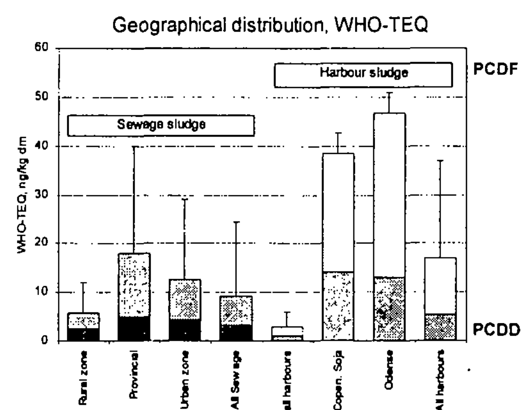

Fig. 4

Fig. 4 shows mean and sd of WHO-TEQ in sewage sludge in geographical zones. The level was unexpectedly highest in the provincial zone (medium size cities), intermediate in the urban zone (large cities) and very low in the rural zone (including small villages). The zone differences are mainly caused by variations in the PCDF-parts. The mean of small harbours is lower than the rural zone, whereas the two selected examples of large harbours, Odense and Copenhagen Soja are much higher and similar. Remarkable, the latter, off a former chloro-alkali plant, lacks the high PCDF level characteristic for chloro-alkali production.

Figs. 5 and 6 show the abundance of selected pollutants in sewage and harbour sludge, respectively, as mean and sd for all samples (logarithmic scale). The most abundant pollutants were DEHP, p-cresol, nonylphenol and phenol in as well sewage sludge as harbour sludge. In harbour sludge the levels of these substances were considerable lower, that of PAH only slightly so, whereas that of PCB was higher.

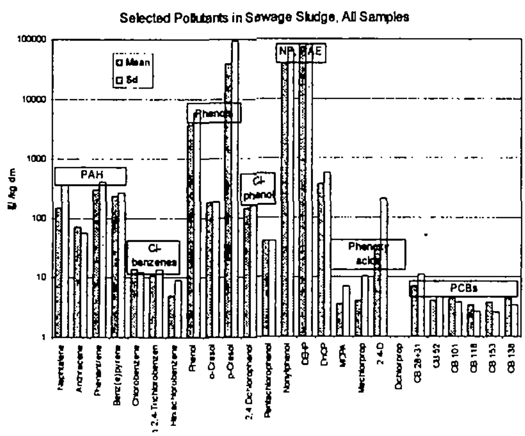

Fig. 5

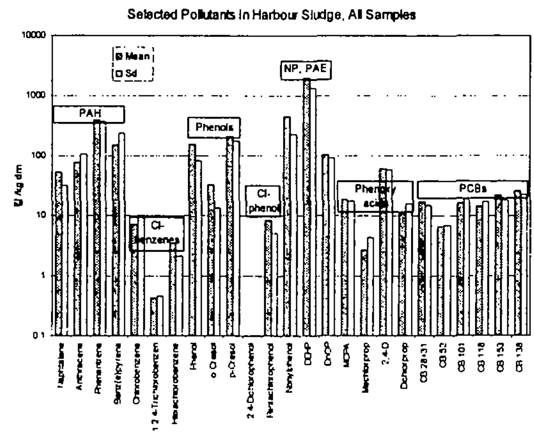

Fig. 6

Significant correlations were found between WHO-TEQ and ΣPAH, Σphenols, ΣNP/PAE and ΣPCB, indicators of the general level of pollution in sewage sludge. Remarkably, no significant correlation with chlorophenols or chlorobenzenes was found, thus these substances do not seem to contribute to PCDD/F. The correlation with PCB is shown in Fig. 7; no linear relationship is seen, but a PCB-maximum occurs about 5 ng/kg WHO-TEQ. The complicated pattern suggests an indirect mechanism, possible formation in the WWTP or elsewhere, perhaps from precursors present[6]. In addition, the geographical difference of the PCDD/F levels suggests the presence of such a factor. Alternatively, the sources are independent of chemicals, such as textile washing[7]. However, this could not be confirmed in a Danish study[8], and disagree with the zone variation.

In harbour sludge the correlations were generally more significant than in sewage sludge. A clear linear relationship between PCDD/F and as well chlorobenzenes as PCB was observed, shown for PCB in Fig. 8. The linearity indicates that the PCDD/F in harbour sludge originate through a simple way, probably from impurities in chlorinated chemicals present.

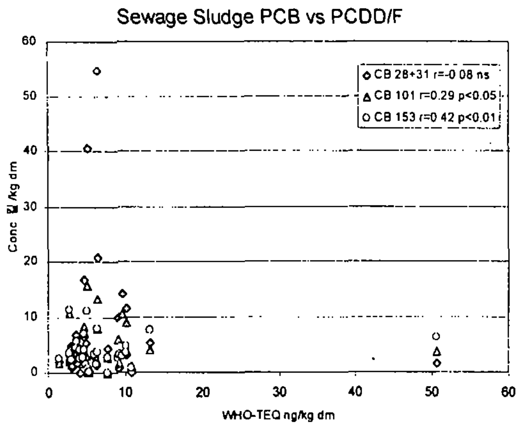

Fig. 7

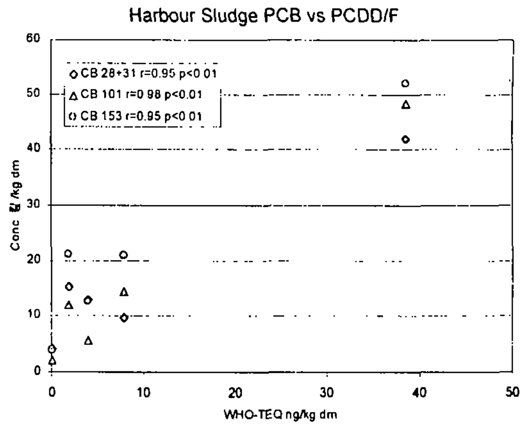

Fig. 8

Conclusions

The results for 38 sewage sludge samples ranged from 1.4 - 51 ng/kg dm WHO-TEQ with mean 9.2 kg dm WHO-TEQ, on level with American and Swedish results. The provincial zone unexpectedly displayed the highest level, the rural zone very low levels. The zone difference and significant correlation between PCDD/F and most abundant pollutants indicates an association with chemical factors. Lack of correlations between PCDD/F and chlorophenols or chlorobenzenes indicate that these substances are not important. Un-linear relationships between PCDD/F and other substances indicate a complicated formation mechanism, or alternatively a source unrelated to chemicals such as textile washing. In harbour sludge, more significant correlations exist than in sewage sludge. PCDD/F were correlated with chlorobenzenes and PCB in a clear linear relationship, indicating a simple route for PCDD/F occurrence, probably from impurities in chlorinated chemicals.

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