ESTIMATION OF THE ENVIRONMENTAL HAZARD OF ORGANOCHLORINES IN PULP MILL BIOSLUDGE USED AS SOIL FERTILIZER

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Introduction. In evaluating the different possible disposal procedures for the increasing amounts of waste biosludge from activated sludge treatment plants of bleached pulp mills, chlorine contamination in the sludge has a central role. All chlorine compounds have to be considered in case of combustion of the sludge. But if the sludge is spread as fertilizer to acricultural, forestry or other soils, especially persistent, bioavailable and toxic organochlorine compounds are important as possible hazard to human health and to the environment.

In several connections, we have analyzed organochlorines in biosludge samples. Detailed procedures and results have been presented in Finnish reports and theses, and part of them will be published later. In the present paper, these results are used as basis to estimate possible environmental hazard of organochlorines from fertilized soil.

Chlorine compounds in biosludge. For total organically bound chlorine (TOCl) in biosludges, levels from 0.05 to 0.2 % in dry matter have been reported[1,2]. Our analyses from kraft mill biosludges gave TOCl contents 0.2-3.25 % and from combination (bark etc. mixed) sludges 0.04-0.6 % dw (dry weight basis). Inorganic chloride contents in these samples were one per cent dw or less.

Majority of the TOCl in sludge is non-bioavailable high-molecular chlorolignin. From the small-molecular toxic organochlorines the best known are chlorophenol compounds and neutral polychlorinated aromatic compounds. Structures of the compounds analyzed are shown in Fig. 1.

Chlorophenolics as hazard. Our recent analyses showed that only about 10 % of chlorophenols in biosludge were extractable by hexane ("free"). The major part of chlorophenols was "bound", extractable with strong alkali. Main congeners in free chlorophenolic fraction were chloroguaiacols which were measured at levels 2-5 µg/g (ppm) dw. The bound chlorophenolics (total 46 µg/g) consisted of 3,4,5-trichlorocatechol (24 µg/g), the other major bound chlorophenolics were PCGs. The free and bound chlorophenols represent about 1 % of TOCl in biosludge.

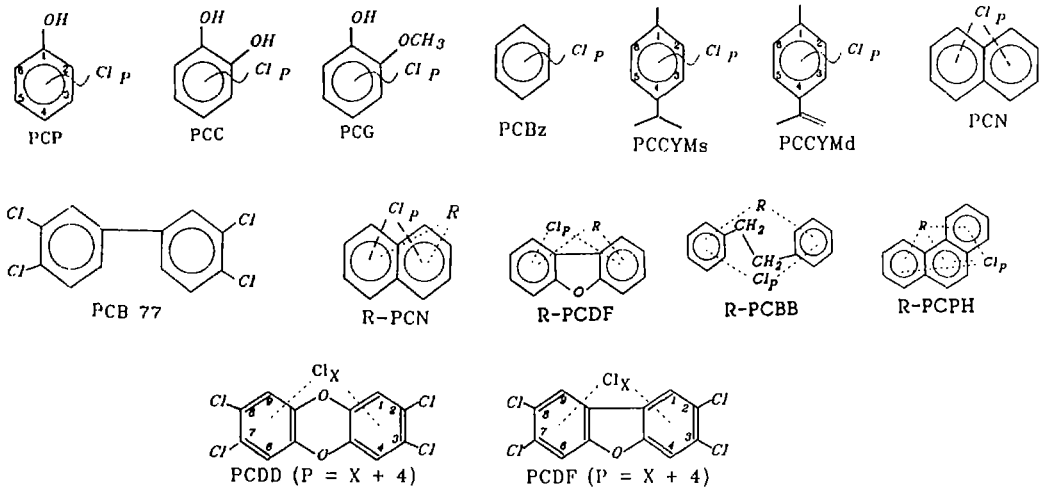

Fig. 1. Structures and name abbreviations of chloroaromatics determined in biosludge:

PCP: PolyChloroPhenols
PCC: PolyChloroCatechols
PCG: PolyChloroGuaiacols
PCBz: PolyChloroBenzenes
PCCYMs: PolyChloroCyMenes
PCCYMd: PolyChloroCyMenenes
PCN: PolyChloroNaphthalenes
PCB 77: Coplanar PCB congener 77
R-PCN: AlkylPolyChloroNaphthalenes
R-PCDF: AlkylPolyChloroDibenzofurans
R-PCBB: AlkylPolyChloroBiBenzyls
R-PCPH: AlkylPolyChloroPHenanthrenes
PCDD: PolyChloroDibenzo-p-Dioxins
PCDF: PolyChloroDibenzoFurans

In soil, the main environmental risk of chlorophenols arises from their leaching to surface and groundwater. In Finland, most incidences have occurred at wood-preserving sites of sawmills, where the levels causing damages have been 500-3500 ppm in contaminated soil[3]. While the biosludges contain only a few ppms of free chlorophenols, the risk of leaching damages from normal agricultural soils feritilized with them is negligible. This hazard could be further minimized with pretreatment by composting where most chlorophenols are degradated[4].

Neutral polychloroaromatics (NPCAs). The notorious 2,3,7,8-substituted PCDDs and PCDFs (Fig. 1) occur in biosludges as totally different isomeric pattern than in municipal sewage sludges[5]. In the latter, Octa-CDD, 1234678-HeptaCDD and Octa-CDF are the dominating isomers. The toxic load as TCDD equivalents (TEQ; Nordic) in one municipal sludge[6] was 37.5 pg/g and in soil fertilized with that sludge 13.0 pg/g dw. In biosludge samples, 2378-TeCDD (TCDD) and 2378-TeCDF (TCDF) are the main congeners: role of the others in TEQ is negligible. In kraft mill biosludges of USA in 1988, average levels 95 pg/g TCDD and 806 pg/g TCDF dw were measured[7]. Our result from a kraft mill waste biosludge sample was 33 pg/g TCDD, 1300 pg/g TCDF and 79 pg/g 123678-HexaCDD, while the other toxic dioxins and furans were non-detectable (< 5 pg/g dw)[8]. As TEQ, this result corresponds 171 pg/g, while the US average is 176 (range 4-256) pg/g.

Levels in biosludges and toxic load estimates for the other NPCAs measured are presented in Table 1.

Table 1. Contents (C) of neutral chloroaromatics (NPCAs) in pulp mill biosludges and approximative TEQs for them.

Compound(s)	C ng/g dw	Ref.	TEF £	TEQ pg/g
Penta-CBz	7.9	¤	.00003	- .24
PCCYMs/d	800 - 1500	¤	.0002	160 - 300
PCB 77	.030 - .66	/8/	.01	.30 - 6.6
PCN	0.70 - 7.0	/8/	.00002	.01 - .14
R-PCDF	264	/10/	.001	- 264
C5-PCBB*	5.00 - 21.0	/8/	.0002	1 - 4.2
R-PCN	5.40 - 7.90	/11/	.0002	1.1 - 1.6
R-PCPH	32.0 - 772.	/11/	.0002	6.4 - 154

£ Interim values based on toxicity data in literature except for PCB 77: value suggested by Safe et al.[9]
¤ Our previously non-published results
* R-PCBBs having five carbons in aliphatic parts

PCCYMs and PCCYMd are from bleaching but PCB from some other contamination. PCNs, R-PCDFs, R-PCBBs, R-PCNs and R-PCPHs are components of dioxin fraction in analysis, called PLACs. All these persistent and bioavailable contaminants are possible dioxin-type of environmental toxicants. TEF values (Table 1) were evaluated from the known accute and chronic toxicity data of PCBz and PCN compounds assuming that increased size and lipophility could elevate toxicity in some extent. As a result, total toxic load from the analyzed neutral chloroaromatics is approximated to be TEQ = 400-700 pg/g dw.

Use of one ton of biosludge per hectare leads to the mixing ratio with soil about 1/200. Then, TEQ of the topsoil would increase about 2-3.5 pg/g, which is not much e.g. near Stockholm, where TEQs in soils for PCDD/Fs only were 9-49 pg/g[12].

For human risk estimation, exposure to NPCAs from soil can be approximated from evaluation done for DDT[13], which has about similar properties than the NPCAs measured in biosludge in average. By calculating combination of all possible exposure routes (consumption of beef, dairy and vegetables being most significant), the DDT exposures as daily intakes (DI) per Kg of human weight are[13]: $DI_{Adults} = 0.00008 \times C$; $DI_{Children} = 0.0004 \times C$, where C is the amount of DDT in Kg of dry soil. NORDIC recommendation of ADI = 7 pg/Kg is reached by children when TEQ in biosludge is 3500 pg/g dw (= VSC; Virtually Safe Concentration). Consequently, the present biosludges applied to soil are below the recommended risk level to humans with safety margin of 5-9. An US evaluation considering only PCDD/Fs leads to VSC as TEQ = 310 pg/g dw in biosludge spread on surface of the forest soil[14].

Hatching success of birds estimated as a sensitive measure of ecological hazard assumes NOAEL in egg 100 pg/g TEQ. This led to VSC 50 pg/g in soil for woodkock which is periodically eating earthworms and earth insects in the treated forest[14]. Consequently, mixing of biosludge 1/200 with soil seems to be ecologically safe, although confirmation with further studies is needed[15].

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