Research Communications

Colloid Facilitated Transport of Polychlorinated Dibenzo-*p*-Dioxins and Dibenzofurans (PCDD/Fs) to the Groundwater at Ma Da Area, Vietnam

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Abstract. PCDD/Fs are hydrophobic organic substances and strongly sorbing to soil particles. Once adsorbed to soil particles they are believed to be virtually immobile. However, research in the last decades confirmed that strong sorbing contaminants may reach the groundwater via colloid-facilitated transport. This pathway has not been investigated before in Vietnam. Ma Da area, 100 km north of Ho Chi Minh City, was repeatedly sprayed during the Vietnam War (1962–1971) with herbicides like Agent Orange containing, beside others, the teratogenic contaminant 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD). 11 surface soil samples and 12 water samples were collected in Ma Da area for analysis of PCDD/Fs in solids. Soil TCDD concentrations ranged from 1–41 ppt with a mean of 8.8 ppt and a mean I-TEQ of 9.7 ppt. Two surface water samples showed colloid bound TCDD (7 and 19 ppt). Groundwater samples showed elevated colloid bound PCDD concentrations (mean 770 ng/kg), mainly octachlorodibenzo-*p*-dioxin. Groundwater colloids separated by filtration did not show any TCDD. The results support that TCDD/Fs can be relocated from the top soil to the groundwater by colloidal pathway. They did not provide evidence that the dioxins bound to groundwater colloids are leftovers from the Second Indochinese War. However, this study reinforces that the colloidal transport pathway has to be included investigating the relocation of strong sorbing organic contaminants.

Introduction. During the Second Indochina War from 1962 to 1971 nearly 80 ML of various herbicides were used to defoliate an area of approx 1.7 million ha in Vietnam. They mostly consist of the butyl esters dichlorophenoxyacetic acid (2,4-D) and/or trichlorophenoxyacetic acid (2,4,5-T), as well as triisopropanolamine salts of picloram and 2,4-D or cacodylic acid (dimethyl arsenic acid) [1]. The phenoxy herbicides contained as by-products polychlorinated dibenzo-*p*-dioxins and –furans (PCDD/Fs), including 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD). After the herbicide application, TCDD is degraded and redistributed through various processes [2,3]. It could be dispersed from the soil surface into deeper layers through bioturbation and ploughing. As PCDD/Fs readily sorb to the soil, they are usually considered to be virtually immobile in the subsurface. To date they are thought to be little danger to groundwater supplies. However, colloids are a major constituent of soils. Soil colloids of organic or inorganic origin can be mobile in subsurface environments. It has been shown that colloids can act as a carrier to facilitate the transport of strongly sorbing contaminants [4]. Even though elevated levels of TCDD have been found in Vietnamese soils and sediments, the possibility of TCDD reaching the shallow groundwater via colloid-facilitated transport has not been investigated before. By no means has this study aimed for a systematic or representative survey of South Vietnam, but to examine if colloid facilitated transport from the topsoil to the groundwater is a potential pathway for the relocation of PCDD/F.

Methods. Soil, groundwater and surface water samples were taken between 15–30 km southeast of Dong Xoai, Binh Phuoc Province, in a triangular area between Xuong Rong (XR), Chan Gia Lake (CG) and Rang Rang village (RR). A reference site (ref) was chosen about 15 km NE of Dong Xoai and 21 km north of Xuong Rong. The reference site did not show a vegetation change attributable to herbicide application either on the ground or on a satellite image [5]. Soil samples (sample prefix S) of ~1 kg were taken at 11 sites including the reference site. Soil samples were air-dried and ground with a tungsten carbide mill. Analysis on all seventeen 2,3,7,8-PCDD/Fs was performed with a Chromatograph/Mass Spectrometer after US EPA Method 1625 (1989). Toxic equivalents (I-TEQ) were calculated using the NATO/CCMC factors [6]. Detection limits ranged from 0.2 ng/kg for TCDD to 0.8 ng/kg for OCDD. Three surface water samples (sample prefix SW) were collected, one each from Chan Gia Lake, a shallow pond, and Ma Da River. Groundwater samples were collected from dug wells (diameter ~1 m, 5 to 20 m in depth) and tube wells (30–60 m in depth). Static water levels ranged from 10–15 m on hilltops to 2–5 m in valleys. Separation of colloids from the water phase was performed with 0.8 µm GF 55 glass fibre papers (Schleicher & Schuell), flushed with isohexane picograde (Promochem). Colloid bound PCDD/F concentrations were calculated based on filtrate volume and the colloid mass retained on the filter. The filtration resulted in colloid mass reduction of >98% (except for GWXR 5.5, which showed only 95.5% reduction) checked by turbidity (Nephla Dr.Lange) and colloid mass analysis (Laser shading, GALAI CIS-1, version 4.3). No PCDD/Fs were found in the filtrate.

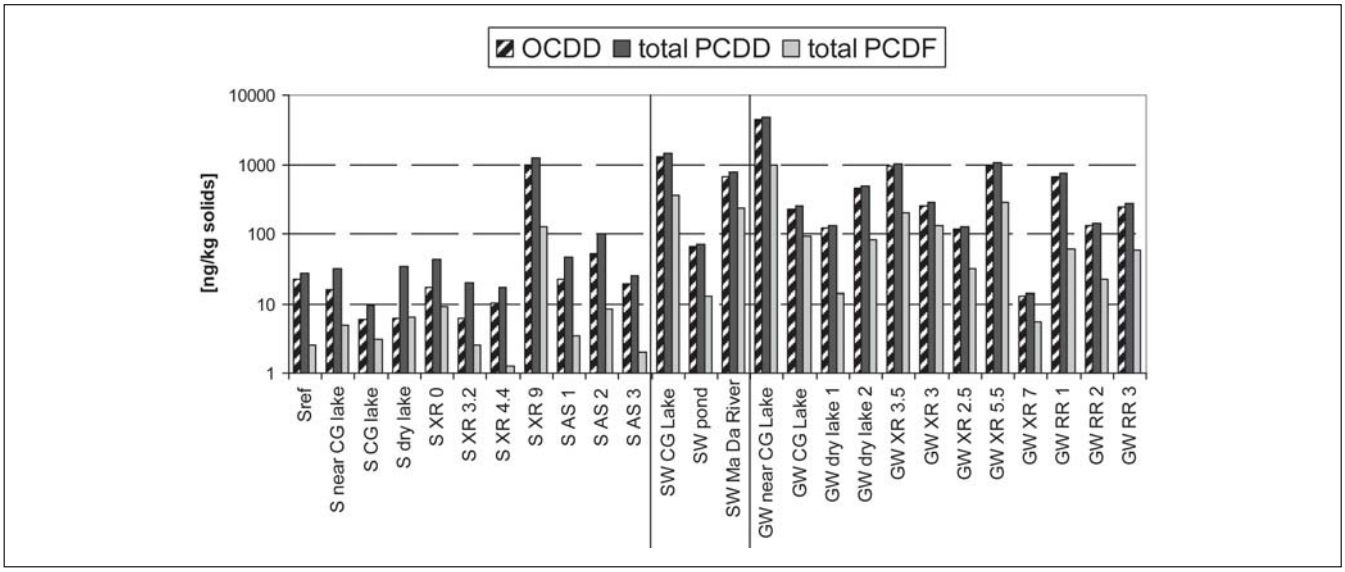

Fig. 1: PCDD and PCDF concentrations in soil (S), surface (SW) and groundwater (GW) samples at Ma Da area. Results of colloid bound PCDD/Fs in water samples are shown as amount per colloid mass. Thus, samples can be compared regardless of their colloid concentration, but PCDD/F concentration per liter of water would be lower for low turbid samples

Results. Apart from the reference sample, all soil samples showed detectable amounts of TCDD (**Fig. 1**), ranging from 1–41 ng/kg (mean concentration 8.8 ng/kg). The mean I-TEQ was 9.7 ng/kg. PCDD/Fs congener profiles were consistently dominated by higher chlorinated PCDDs, in particular OCDD. PCDDs accounted for 75–93% and OCDD for 15–70% of the total PCDD/Fs concentrations in the samples. Colloid concentrations of the groundwater samples were high with a mean of 65 +/– 56 mg/L (range from 2.6 to 173 mg/L).Only two surface water samples (SW_{CGLake}, $SW_{MaDaRiver}$) showed detectable levels of colloid bound TCDD of 19.3 and 6.6 ng/kg colloid mass, respectively, while none was detected in any groundwater sample (see Fig. 1). Colloid bound PCDD levels were high for all water samples with a mean of 770 ng/kg colloids, dominated by OCDD (mean of 90%). PCDF levels were approx. five times smaller and also dominated by higher chlorinated homologues (on average 92% for sum of heptachlorinated dibenzofuran (HpCDF) and octachlorinated dibenzofuran (OCDF)). $GW_{nearCGLake}$ showed an extreme value for OCDD (4,380 ng/kg) and reached 18.9 ng/kg I-TEQ, whereas most of the other groundwater samples were below 4 ng/kg I-TEQ.

Discussion. The high TCDD concentration at Chan Gia Lake could be explained by accumulation of fine material in the lake from the surrounding area over the years. Elevated TCDD levels in Ma Da River are a sign of present soil contamination in the catchment area. There was no colloidal TCDD detected in groundwater samples. These results indicate that TCDD has not reached the groundwater body by colloidal transport at the sampling sites. However, all groundwater samples showed other colloidal PCDD/Fs, with a dominance of highly chlorinated ones. This confirms that colloidal transport of hydrophobic organics contaminants is a pathway that has to be taken into account. To identify exactly the source of the elevated OCDD concentrations, and why OCDD but not TCDD can be found in groundwater samples, a detailed analysis of the colloids itself is needed. This can only be done by modern sophisticated colloid detection techniques, e.g. dynamic and static light scattering, field flow fractionation coupled with MS, laser induced breakdown detection, and was out of the scope of this study.

Conclusion. It was found that in this region heavily sprayed with herbicides a considerable amount of TCDD is detected in all soil samples, except for the reference site. TCDD was found in two surface water samples, which supports the contamination of the area. Besides spraying missions, fires at Ma Da forest have to be taken into account explaining the relatively high PCDD soil concentrations. In groundwater samples high colloid concentrations were found. Linked to these colloids were elevated colloidal OCDD concentrations, but no TCDD. Thus, colloidal transport of PCDD/Fs can be observed at the investigated area, but from this study there is no evidence that these dioxins are from spraying missions during the Second Indochinese War. High OCCD levels could be a sign of forest fires at Ma Da area. Due to the very low concentration colloid bound PCDD/Fs in groundwater samples examined in this study do not pose a health risk; however, a more detailed study of the origin of the high OCDD concentrations is desirable.

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