Facilitated Transport of Dioxins in Soil Following Unintentional Release of Pesticide-Surfactant Formulations

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Colloids such as surfactant micelles can act as transport facilitators for highly lipophilic, generally immobile contaminants in soil. Following a fire at a pesticide facility, this study investigated vertical and lateral migration of polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs) in heterogeneous soil beneath bunded ponds, where contaminated wastewater containing high surfactant loads was stored until remediation. Initially, surface and subsurface soil was obtained during excavation, and subsequently intact cores to 5.7 m were collected. ∑PCDD/F concentrations were elevated in the wastewater (15–81 ng/L) and correspondingly in pond surface soils (6.1–61 ng/g). Maximum ∑PCDD/F concentrations were, however, observed at 2–2.5 m depth (68–130 ng/g), far below their expected mobility range based on physicochemical properties. Congener specific analysis further indicated that PCDD/F mobility was reversed, with the least water-soluble congeners migrating to the greatest extent. The presence of higher chlorinated PCDD/Fs throughout a core collected in the direction of groundwater flow indicated subsequent lateral transport. These results provide field evidence for rapid vertical migration (2.4 m in <4 months) of highly lipophilic PCDD/Fs and suggest surfactant facilitated transport as the dominant transport mechanism. Quantification and evaluation of such fundamental changes in contaminant transport and fate in the presence of surfactants is required to identify areas at risk of groundwater contamination.

Introduction

The transport potential for chemicals in deposition matrices such as soil and sediments is strongly dependent on their water solubility and affinity for soil organic matter. Hydrophobic organic chemicals (HOCs), which have low water solubility (S_w) and high organic carbon—water partitioning coefficients (KOC), have previously been considered to be immobile in such matrices (1). However, several studies have shown that the presence of synthetic or natural colloids (e.g., surfactant micelles, biosurfactants, organic matter, humic substances) or other cocontaminants (e.g., oils, solvents) may enhance HOC transport in porous media by increasing their apparent aqueous solubility (1–3). As a result, faster and increased fluxes of HOCs may reach groundwater compared to transport in the absence of such ‘facilitators’ (4), with an associated risk of off-site migration. For facilitated transport to be significant, it has been recognized that the facilitators, which can be dissolved or suspended in soil—water, must be present at sufficiently high concentrations and be mobile in the porous medium, and HOCs must associate strongly with the facilitating species (5). For surfactants, facilitated transport is expected to occur most effectively at surfactant concentrations above the critical micelle concentration (CMC) (3). At CMC, surfactants aggregate into micelles which can readily transport with the aqueous phase via their hydrophilic surface layers, while nonpolar contaminants can partition into their hydrophobic cores. In a soil—water system, sorption of surfactants to soils increases the concentration required to achieve aqueous CMC (and hence micelle formation), and the extent of sorption is dependent on soil properties, such as organic carbon content, and surfactant type. The transport potential of HOCs with surfactants is therefore determined by the characteristics of the soils, water flow, surfactants, and HOCs involved (6).

Enhanced HOC transport with facilitators may be occurring across a variety of land-use areas. For example, immobile pesticides (e.g., DDT, trichloroacetic acid, parathion), polycyclic aromatic hydrocarbons (PAHs) and polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs), in the presence of surfactants and other colloids has been demonstrated in laboratory soil column leaching experiments and to a lesser extent in lysimeter studies (2–4, 6, 7). In addition, the concept of solubilization and mobilization of soil-sorbed contaminants through injection of high concentrations of surfactants is being successfully applied as innovative technology for remediation of contaminated soils (8, 9). Outside of such specialist and controlled applications, however, there are remarkably few field studies investigating this process in situations where surfactants may be released at high loads and/or high frequencies under less controlled conditions (e.g., during industrial accidents, chemical spills, or via application of pesticides, biosolids, or irrigation waters) (10).

Enhanced HOC transport with facilitators may be occurring across a variety of land-use areas. For example, immobile pesticides (e.g., DDT, parathion, methoxychlor, dichlorvos) have been observed at several meters or in groundwater below agricultural and other soil (11–13) and at pesticide/chemical production facilities (14–16) as well as PAHs at depth in agricultural soils (17) and in groundwater at coal-tar sites (e.g. ref 4). Similarly, the highly hydrophobic PCDD/Fs have been detected at elevated levels at several meters in soils or in groundwater such as in Australian agricultural and forest soils (18, 19), at former wood treatment sites in Sweden and the US (20, 21), at German pesticide production facilities (10), in Agent Orange contaminated soils in Vietnam (22, 23), and beneath landfill sites in Korea and elsewhere (e.g. ref 24). One of the main difficulties for field studies such as these, which report the presence of HOCs in groundwater or soils at depths far below their predicted mobility, is to elucidate the mechanism or facilitators resulting in these field observations. In specific cases where HOCs were demonstrated to be associated with the natural colloidal fraction of groundwater, colloids in the form of dissolved or particulate organic matter have been considered to represent the responsible facilitators (4, 21, 22). While surfactants may often be present in soils, they are significantly less persistent in the environment than many HOCs, in...
particular PCDD/Fs which have half-lives in soil in the order of decades. As a consequence, the role of surfactants as contaminant transport facilitators can rarely be investigated in the field retrospectively.

This study describes the vertical and lateral migration of PCDD/Fs in soils recently contaminated following an unintentional fire at a pesticide manufacturing and formulation facility. High volumes of pesticide formulations and their combustion products were released in the fire extinguishing water as surface runoff. This wastewater, which was retained in bunded containment ponds until remediation, contained elevated concentrations of pesticide mixtures and PCDD/Fs as well as known transport facilitators (mixtures of anionic and nonionic surfactants used as adjuvants in pesticide formulations). This site provided an opportunity for field investigations to 1) assess whether facilitated transport of HOCs occurred and the associated extent and rate of vertical migration, 2) evaluate this process with respect to PCDD/F congener physicochemical properties, and 3) examine the potential for lateral offsite movement of PCDD/Fs in the direction of groundwater flow.

**Experimental Section**

**Site and Sampling Details.** In August 2005 a fire at a pesticide manufacturing and formulation plant near Brisbane, Australia, resulted in the release of fire extinguishing water (not foam) mixed with pesticides, adjuvants, combustion products, and impurities. The associated wastewater flowed rapidly (∼200 m downhill (~4% slope) to an ephemeral creek which was not flowing prior to the fire. Four bunded containment ponds (ponds 1 to 4) were constructed in the original creek bed to retain wastewater runoff, and an artificial bypass for the creek was established adjacent to these ponds (Figure S1-Supporting Information (SI)). The wastewater was retained in the ponds until contaminated water was removed and soil excavated (2–3 m depth) for remediation over the following 3 years.

Samples of pond water (i.e., wastewater), surface, and subsurface soils were collected during remediation activities over the two years following the fire (see timeline, Figure S2–SI). Between 7–10 months after the fire when the ponds were drained, wastewater from ponds 1 and 2, and composite soil samples from the surface layers of all four containment ponds were obtained and analyzed for PCDD/Fs by the Department of Environment and Resource Management (DERM) (25). Between 19–20 months after the fire when the ponds were excavated, composite soil samples were obtained at an excavation depth of approximately 2–3 m from ponds 2, 3, and 4. All surface- or subsurface-excavated soil samples were composites of 10–15 subsamples, collected with 10 cm solvent-washed aluminum cores. Subsamples were amalgamated, homogenized, and stored frozen until analysis.

Based on initial findings of elevated PCDD/Fs in the composite soil samples, three intact cores to 5.7 m depth were collected 23 months after the fire using a Geoprobe model 6610DT coring machine and macrocore sampling system. The coring was undertaken according to standard procedures and resulted in visually intact soil cores. Coring sites were located in ponds 1 and 4 (cores P1–4) and the bypass creek (core C4) adjacent to and approximately 10 m distant from pond 4. Prior to coring, pond 4 had been excavated to a depth of approximately 2 m and backfilled with clean soil. The top 2.3 m of core P4 was therefore discarded, and only soil below this depth was analyzed. Similarly, the top 0.5 m of core C4 was discarded as a protective, impervious liner had been laid along the constructed creek bed at this depth.

Geoprobe cores were collected using multiple sections of clean, transparent PVC barrel liner tubes measuring 1500 mm in length and 50 mm internal diameter. The tubes were transported to the laboratory for further processing. To avoid cross contamination between and within cores throughout sample preparation and analysis, the PVC tubes were opened using a solvent-cleaned knife and after careful removal from the tube, soils were divided into 10 cm sections which were individually wrapped in aluminum foil and stored frozen prior to further processing and analysis. Further, core sections to be analyzed were defrosted, and the outer 2–4 mm of soil were removed to ensure any cross-contamination was excluded. The remaining soil was homogenized using a solvent-cleaned mortar and pestle. A 100 g subsample was taken from each core section, freeze-dried, and sieved to remove particles >2 mm.

**Sample Extraction, Cleanup, and Analysis.** Sample extraction, cleanup, and analysis of tetra- to octa-chlorinated dioxins and furans followed U.S.EPA method 1613 (isotope dilution method using HRGC/HRMS), and is described the SI (Section S1). At the time of core sampling, the less persistent pesticides released in the wastewater (e.g., 2,4-D, chlorpyrifos, MCPA, dichlorvos) were no longer present at quantifiable levels.

Total organic carbon (TOC) was determined at Queensland Health laboratories (QHFSS) according to a NATA (National Association of Testing Authorities) accredited standardized procedure. In brief, inorganic carbonates were removed using acid digestion, and the remaining material was dried and combusted in a LECO induction furnace with subsequent detection of CO₂. Total water-soluble anionic surfactant concentrations were determined as methylene blue active substances (MBAS) at QHFSS according to a NATA accredited method. In brief, soil samples were extracted with MeOH. Filtered extracts were purified using sublation to remove nonsurfactant substances. Extracts were transferred to water and reacted with methylene blue reagent. Anionic surfactant-methylene blue reaction products were extracted three times with chloroform, an aqueous backwash was performed, and the color was measured spectrophotometrically at 652 nm. Particle size analysis was performed using the pipet method at the Atmospheric Environment Research Centre, Griffith University according to standard procedures as described in ref 26.

**Quality Assurance/Quality Control (QA/QC).** Identification and quantification of congeners followed U.S.EPA method 1613. A summary of the QA/QC process and the QA/QC measures for this study and information on identification of non-2,3,7,8-substituted congeners is included in Section S1–SI.

**Results and discussion**

**Vertical Migration of PCDD/Fs below Containment Ponds.** Monitoring results by DERM showed that elevated concentrations of ΣPCDD/Fs were present in the containment pond water (15,000–81,000 pg/L (25)). Surface soil from the ponds, collected after the water in the ponds was drained, reflected this contamination (6100–61,000 pg/g) (see Figure S2–SI for sample collection timeline) (25). The very hydrophobic PCDD/Fs (logKow = 5.8–8.3, logKow = 5.7–7.9, Sow = 1.5 × 10⁻⁷–3.6 × 10⁻⁴ mol/m³) contained in the pond water were expected to bind strongly to the organic carbon (OC) in the surface layers of the pond soils, particularly as surface soils had higher OC loadings compared to deeper layers (Table S1–SI). However, PCDD/F concentrations remained elevated (ppb levels) throughout the top 3–4 m in all cores (Figure 1; Table S1–SI). Furthermore, ΣPCDD/F concentrations were observed to increase with depth, with maximum concentrations, on average 5 times greater than at the surface, at a depth between 2–2.5 m in ponds 1, 2, and 4 (130,000 pg/g dw at 2.4 m depth, 72,000 pg/g dw at 2 m, and 94,000 pg/g dw at 2 m, respectively). Insufficient samples were available from pond 3 to determine where the maximum concentration occurred, although ΣPCDD/Fs were also elevated below the surface (35,000 pg/g dw at 3 m). Below 2–2.5 m, ΣPCDD/F
concentrations decreased relatively rapidly to ppt levels at approximately 5 m depth.

Uncontrolled fires of chlorinated chemicals are well recognized to result in the formation of elevated PCDD/Fs. The resulting PCDD/F profile is specific to the mixture of chemicals (PCDD/F precursors) present and the conditions during the fire (29). In addition, it has been shown that commonly used pesticides, including those released during the fire, contain PCDD/F impurities (30), with profiles specific to their active ingredients and manufacturing conditions. Due to the high concentrations of PCDD/Fs in the pond water, i.e. wastewater sourced from the fire at the facility, it can be concluded that the associated PCDD/F profile reflects this mixture of particular sources, conditions, and formation processes. The PCDD/F profiles were dominated by octachlorinated dibenzo-p-dioxin (OCDD) (range 85–99% of ΣPCDD/Fs) with decreasing concentrations toward lower-chlorinated 2,3,7,8-substituted congeners and homologues (HpCDD > HxCDD > PnCDD≈TCDD) (Table S1–SI). In contrast to PCDDs, concentrations of most PCDF congeners were relatively low or below the limit of quantification (LOQ) with the notable exception of ΣTCDFs, in particular 2,4,6,8- and 1,3,6,8-substituted isomers (Figure S3–SI). The PCDD/F profiles throughout the pond soils were almost identical to those of the wastewater (Figure S3–SI) and contained similarly elevated concentrations, indicating the contamination originates from the same source/formation process. In addition, surface soil surrounding the ponds showed notably different PCDD/F isomer profiles (Figure S3–SI), further suggesting that the contamination of the ponds was caused by the chemical fire. A more detailed description of the PCDD/F homologue, congener and isomer profiles, and comparison to known source profiles is provided in the Supporting Information (Section S2–SI and Figure S3–SI).

Organic compounds can move with soil–water either as truly dissolved species or sorbed to facilitators. In the dissolved state, rapid transport of HOCs may be possible under conditions of preferential flow, where a large proportion of water flow by-passes the bulk soil matrix in preferential flow paths (e.g., channels or fissures) and sorption processes are reduced (31). However, only very low concentrations of the extremely hydrophobic PCDD/Fs can be dissolved (i.e., requiring exceptionally high volumes of contaminated water to transport high PCDD/F loads). Results of this study show that relatively high concentrations and loads of PCDD/Fs were sorbed throughout the soil profile (Figure 1). In addition, preferential flow is characterized, and often identified, by a lack of chromatographic separation of contaminants through the soil profile (31), which contrasts with the present results (see below). Hence, although preferential flow may have occurred at the site, it was unlikely the dominant transport process considering that matrix flow must have occurred for a substantial proportion of PCDD/Fs. This suggests that a carrier was necessary to facilitate transport in soil–water.

Both natural soil colloids and surfactants are possible transport facilitators at this site. However, the low organic carbon content of the soils suggests a relatively low availability of natural soil colloids, compared to the high surfactant loads that were present. In addition, a decrease in colloid concentration (and thus sorbed contaminants) in soil–water with travel distance is predicted under the classical colloid filtration and subsequent theories (5, 32). The PCDD/F concentration profiles in the cores of the present study (i.e., with surfactant-facilitated transport) are consistent with this pattern, further suggesting that natural soil colloids were unlikely to be the principal facilitators at this site. The observed ΣPCDD/F concentration profile with depth in the pond cores is, however, consistent with surfactant-facilitated transport. No correlations were found between PCDD/F profiles and OC levels in the soils (Figure S4–SI) or with soil pH or clay/sand/silt content (Table S1–SI). However, the shallow aquifer at the study site was measured at 0.5–2 m depth across the ponds during the fire (33). Under surfactant-facilitated transport conditions, surfactant dilution upon reaching groundwater is expected to result in micelle disaggregation and sorption of PCDD/Fs to soil particles (and to surfactants sorbed to soil). Consequently, at least a portion of PCDD/Fs would be expected to be retained at groundwater depth in the period following the fire. Thus, the observed PCDD/F concentration profile suggests that the extent of surfactant-facilitated transport was restricted to the vadose zone, and below this level, in groundwater, surfactants may not have been present consistently above CMC to facilitate transport of PCDD/Fs to the same extent.

Stock records from the pesticide facility showed that high volumes (>28,000 L) of 20 different anionic and nonionic surfactants (commonly used in pesticide formulations) were stored on-site prior to the fire. The highest volume surfactant types were the anionic linear alkylbenzene sulfonate (LAS), 13% of the total volume; alkybenzenesulfonate (AOS), 8%; and alkylphenol ethoxylates (APE; 26%) and alkylamine ethoxylates (8%). These types were the anionic linear alkylbenzene sulfonate (LAS; 13%) stored on-site prior to the fire. The highest volume surfactant types were the anionic linear alkylbenzene sulfonate (LAS), 13% of the total volume; alkybenzenesulfonate (AOS), 8%; and alkylphenol ethoxylates (APE; 26%) and alkylamine ethoxylates (8%). These types were the anionic linear alkylbenzene sulfonate (LAS), 13% of the total volume; alkybenzenesulfonate (AOS), 8%; and alkylphenol ethoxylates (APE; 26%) and alkylamine ethoxylates (8%). These surfactants, in the order of up to 10,000 ppm, would have been present in the pond water immediately after the fire. This is comparable to the high concentrations used for surfactant enhanced remediation at contaminated sites (9). To achieve mobilization of HOCs in soils, it has been shown experimentally that CM_{eff} (or as an alternative measure the concentration at which HOCs are leached in soil column outflow experiments) for LAS is ~1500 ppm (7) and for AEs and APEs in the range 500–1000 ppm (34). CM_{eff} is dependent on soil properties which determines the extent of surfactant sorption to soil; however, the low organic carbon of the current study soils.
(<0.05—1.8% TOC, median 0.05%, Tables S1,S2—SI) suggest comparatively low sorption losses. In addition, reduced CMCs have been reported for anionic/nonionic surfactant mixtures compared to individual surfactants as mixed micelles are formed (8), implying 1500 ppm represents a conservative estimate of total surfactant concentrations required to achieve PCDD/F mobilization at this site.

Using a simple model based on the estimated initial surfactant concentrations and reported half-lives for LAS and AEs (see Section S3—SI and Figure S5—SI for details), total surfactant concentrations at the study site would have remained above $\text{CMC}_{\text{eff}}$ (∼1500 ppm) for an estimated ∼130 days. Transport rates of PCDD/Fs with surfactant micelles depend on hydrological conditions at the site. A simulation of the vertical water flow using HYDRUS-1D (35), based on water ponding heights, precipitation data, and soil properties, provides an estimate of the water flux at the study site (see Section S4—SI for details). This suggests the breakthrough of pond water at 2.4 m depth to commence within 2 days and peak after 110 days (driven by subsequent precipitation) (Figure S6—SI). A retardation effect, based on soil properties and sorption isotherms between soil, contaminants, and surfactants, slows the PCDD/F migration rate relative to the flow rate of the surrounding water, and once surfactants had degraded to below CMC, sorption of PCDD/Fs to the soil matrix would likely limit further movement. We can therefore tentatively conclude that the vertical PCDD/F profile observed at the study site reflects the cumulative result of contaminant movement with surfactant micelles during infiltration of pond water, and subsequent vertical movement under gravity and rainfall, for a period up to ∼4 months. This suggests a minimum rate of vertical PCDD/F migration under matrix flow in the order of 0.5 m per month. The conditions of the current study site may be comparable to scenarios where application of pesticides (with surfactants above CMC) is followed by intensive irrigation or high intensity rainfall.

However, where surfactant sorbed PCDD/Fs are carried with water through preferential flow paths transport could be significantly faster. Conversely, slower rates for facilitated PCDD/F migration would be expected in areas where the soil infiltration capacity is not exceeded (i.e., under non-ponded conditions).

**Congener Specific Migration Potential in the Vadose Zone.** According to partitioning theory, a small fraction of PCDD/Fs will be truly dissolved in soil–water. Under these conditions the more water-soluble, i.e. lower chlorinated, congeners have the greatest transport potential. In contrast, results of the present study indicate that the most hydrophobic congener OCDD (log$_{10}$KOC = 7.9, $S_W = 2.8 \times 10^{-6} \text{ mol/m}^3$ 28, 29) was preferentially mobilized compared to lower-chlorinated, less hydrophobic compounds such as TCDDs (log$_{10}$KOC = 6.5, $S_W = 1.0 \times 10^{-4} \text{ mol/m}^3$ 27, 28) (Figure 1). Despite the overall and striking similarity of PCDD/F patterns in all samples, congener and homologue profiles were observed to shift slightly, but progressively, toward more hydrophobic congeners with increasing core depth in the top 2.5 m (i.e., the vadose zone). For example, in pond 1 (where sufficient numbers of samples are available to allow trend analysis), the contribution of OCDD to $\Sigma$PCDDs showed a continuous increase with depth through the core samples ($r^2=0.96$; Figure S7—SI), whereas the contribution of lower-chlorinated congeners such as $\Sigma$TCDDs and $\Sigma$nCDDs decreased ($r^2=0.91$ and 0.81, respectively; Figure S7—SI). The surface soil sample, which was collected after the ponds were drained approximately one year prior to collection of the core, contained lower contributions of lower-chlorinated PCDDs compared to the pattern observed in the cores, possibly as a result of volatilization loss processes in subtropical air temperatures after pond drainage (Figure S7—SI). The gradual PCDD concentration and profile shifts indicate a fractionation of dioxins through this region of the core and suggests that vertical transport associated with
suggests that a greater proportion of the higher-chlorinated PCDD/Fs may have undergone lateral (subsurface) migration from pond 4, suggesting that a substantial proportion of contaminant patterns in the creek core were similar to those below 2.5 m depth of the impervious material were likely sourced via horizontal, subsurface inflow from the adjacent ponds. Elevated levels of ΣPCDD/Fs were found in the creek core with maximum concentrations of 18,000 pg/g at 3.6 m depth (Figure 1; Table S2—SI). In addition, homologue and congener profiles throughout the creek core were similar to those in the pond soils and in particular reflected the deeper pond layers (i.e., lower-chlorinated PCDD/Fs, which were detected in surface layers of pond 4, were below LOQ even in the top creek core layers) (Figure S8—SI). The presence of PCDD/Fs throughout the creek core, and their identical PCDF congener patterns compared to the deeper (>2 m) layers of the adjacent pond 4, suggest that migration with subsurface lateral groundwater flow occurred. Changes in water table height with seasonal rains may further be expected to have the potential for PCDD/Fs to infiltrate subsurface creek soils at varying depths via this pathway. Groundwater flow rate at the study site is approximately 2.1 m/month (33) which is the maximum lateral flow rate that transported contaminants could achieve. Thus, it seems reasonable that PCDD/Fs could have traveled the 10 m distance to the creek core site within the 23 months since the fire. PCDD/F concentrations in the creek core were similar to those below 2.5 m from pond 4, suggesting that a substantial proportion of PCDD/Fs may have undergone lateral (subsurface) migration.

**Information Gaps and Implications.** The majority of investigations on surfactant-HOC interactions in soil have been carried out under controlled and extreme (high level) conditions applicable to desorbing existing contaminant loads with surfactant based remediation techniques. However, such interactions are highly complex and cannot be readily predicted at present for conditions where surfactant-HOC mixtures are released together as at the present study site or intentionally but at lower levels over prolonged periods. Several factors have been shown to significantly affect the rate and extent of surfactant-facilitated migration of HOCs in soil column experiments, including hydrological conditions (e.g., ponding, rainfall intensity and duration), soil properties (e.g., TOC and clay content, hydraulic properties, CEC, pH), the type and mixture of surfactants present, and properties of the HOCs themselves (e.g., water solubility, lipophilicity, molecular size) (1, 8). Thus, the extent of surfactant-facilitated transport is likely to be site/location specific. In addition, most research into surfactant solubilization of contaminants considers single-surfactant (8) or single-contaminant (39) systems or equilibrium conditions with excess solute (40), which are unlikely to reflect actual circumstances at surfactant-HOC release sites. For example, few studies have investigated the mechanisms governing competitive behavior between HOCs in mixtures with different surfactants under nonsteady state conditions, where competitive, neutral, and synergistic effects on solubilization between contaminants have been described (39, 40). The consequence of the current information gaps regarding the potential for this transport pathway to occur in the environment may be unrecognized or unexpected groundwater contamination and potential off-site transport of contaminants.

In this respect it is noteworthy that previous field observations suggest that enhanced PCDD/F mobility may be occurring in some agricultural soils, where a mixture of surfactants are applied repeatedly as part of agrochemical formulations and/or irrigation wetters. For example, OCDD and HpCDD congeners (2.8–1500 pg/g) were found to 1.5 m depth in sugar cane soils (19). Similarly, exclusively higher-chlorinated PCDD congeners (6.8–24,000 pg/g) were observed up to 3.5 m depth in forest soils directly adjacent to a pineapple plantation, where surface soil contained elevated concentrations of other lower-chlorinated congeners characteristic of the fungicide and wood preservative pentachlorophenol (PCP) (18). These findings of exclusively higher-chlorinated PCDD/Fs in deep soil layers are consistent with the observed reversed mobility of the present study and suggest facilitated transport may have occurred. Surfactants have not been considered previously as potential facilitators at such sites, although they are commonly included in pesticide formulations at concentrations well above CMCeff (typically 1–10% v/v or 10,000–100,000 ppm) (6). It is generally expected that desorbing existing contaminants concentrations fall to below aqueous CMC in soil—water, via dilution with rainfall/irrigation, or through sorption losses to soil (1). However, field investigations on HOCs and/or surfactants in agricultural soil cores are scarce, and few studies have investigated transport of HOCs when applied together with surfactants (as opposed to desorbing existing HOC loads from contaminated soil). Further, the effect of surfactant mixtures, the presence of cofacilitators in the soil system, and repeated (i.e., potentially cumulative) applications of surfactants to achieve CMC are largely unknown.

Surfactants are typically considered to be inert substances, and their influence on contaminant transport and fate is rarely taken into account (38). The present study highlights that persistent organic compounds generally considered immobile in the environment, such as PCDD/Fs, have the potential to migrate rapidly and to substantial depths when released together with high concentrations of surfactants. This potential for surfactants to fundamentally change contaminant behavior in soil should be carefully considered in areas where high loads of surfactants are released intentionally or unintentionally, to facilitate protection of groundwater resources.
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Supporting Information Available
PCDD/F concentrations in soils/cores, isomer elution order, site map, sampling timeline, PCDD/F isomer profiles for wastewater, pond and local soils, PCDD/F concentrations on TOC basis, % change in OCDD, ΣPnCDDs and ΣTCDDs with depth; plus additional information on analytical methods, PCDD/F profiles and formation, surfactant half-life model, and HYDRUS-1D simulation of water flow. This material is available free of charge via the Internet at http://pubs.acs.org.

Literature Cited
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