Land Contamination by Chlorinated Dioxins and Furans: a Brief Overview of Causes, Effects and Solutions

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The dioxins and furans constitute arguably one of the most problematic areas of land contamination because of their widespread nature and environmental recalcitrance. The exceptional toxicity of the group means that they are of concern at very low levels, so sophisticated and expensive monitoring and remediation techniques are required. Sources of PCDD/Fs within the chemical manufacturing industry are well characterized so potentially contaminated sites can easily be identified on a process basis. Accidental releases and landfilling of wastes are also major causes of land contamination. Humans may be exposed to soil-associated dioxins either through direct contact and indirectly through consumption of dairy products from cattle grazed on contaminated land. This article provides an introduction to some of the causes and effects of contamination of land, and the extent of knowledge in the UK. The past and future options for clean-up operations are also discussed.

INTRODUCTION: DIOXINS AND FURANS

Polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) are groups of 75 and 135 compounds respectively. The entire group can be referred to as PCDD/Fs or, more loosely, the dioxins. The basic structure of the PCDD or PCDF molecule is constant, and the different members of the group (congeners) vary in that they contain up to eight chlorine atoms differently arranged. The most toxic 17 congeners have chlorine atoms at the 2,3,7 and 8 positions and 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD or TCDD) is perhaps the most toxic compound ever manufactured. Its toxicity to animals is undisputed and a range of effects to humans are emerging, as discussed below.

Dioxin results are generally reported in one of three ways:

(a) 2,3,7,8-TCDD, the single most toxic congener may be reported alone;

(b) 2,3,7,8-TCDD toxic equivalents (TEQ), calculated from the concentrations of the most toxic 17 congeners may be reported; or

(c) the total concentration of all dioxin and furan congeners may be used. Current practice is generally for TEQs to be reported, though older data are often restricted to 2,3,7,8-TCDD concentrations. Reporting total PCDD/F concentration is of limited utility because it gives no indication of the toxicity of the mixture.

BEHAVIOUR IN THE SOIL

Dioxins are extraordinarily stable; residues have been detected in tissue and sediment samples thousands of years old (Hashimoto *et al* 1990; Schecter *et al* 1988). They are semivolatile and hydrophobic and so partition to soil readily, particularly soils with a high component of clay or organic matter. This affinity for soil prevents them being easily leached or biodegraded. At Seveso in Italy, 2,3,7,8-TCDD remained in the top 8 cm of soil for the first year (Arthur and Frea 1989). Other research gives the half-life of PCDD/Fs in soil as between one and ten years, due to volatilization rather than degradation (Arthur and Frea 1989). In experiments, only 1.3% of pentachlorodioxin applied to the surface of soil leached to the depth of 2-5 cm over a period of 21 months (Friesen *et al* 1990). Over the same time period only 0.9% was recovered as extractable degradation products. The greatest loss from soil – some 70% – was by way of volatilization.

INDUSTRIAL CONTAMINATION BY PCDD/FS

Table 1 lists a number of industrial processes which have been identified as routinely generating dioxin-containing wastes. The sites of these industries would be likely to have soil contamination and therefore should be priority cases for investigation, as should dumps and landfills containing waste from these processes. Wide variations in the severity of on-site contamination are to be expected. In Germany, industrial (non-combustion) sources are listed in order of priority as follows (Heidl and Hutzinger 1986):

1. processes involving chlorophenols;

2. processes involving chlorobenzenes and further substi-

tuted chloroaromatic compounds;

3. synthesis of aliphatic chlorine compounds;
4. processes where chlorine is part of the molecule in intermediate stages but not part of the final product;
5. processes of inorganic chlorine chemistry;
6. processes involving chlorine containing catalysts and solvents.

Table 1. Industrial processes generating dioxins and furans*

Production of chlorine by mercury cell
Production of vinyl chloride monomer
Processes involving chlorophenols
Processes involving pentachlorophenol
Production of organochlorine pesticides: 2,4-D, 2,4,5-T, lindane
Processes involving aromatic or aliphatic organochlorines
Production, use and incineration of PCBs
Municipal waste incineration (including PVC incineration)
Hazardous waste incineration
Chlorine paper bleaching processes
Magnesium smelting
Nickel smelting
Scrap metal smelting
Steel smelting
Copper wire recycling
Oil refining
Drycleaning processes using perchloroethylene

* (Bopp *et al* 1991; Cull *et al* 1983; Cheng *et al* 1990; Erickson *et al* 1989; Oehme *et al* 1989; Tysklind *et al* 1989; Harnly *et al* 1990; Marklund *et al* 1990; Fiedler *et al* 1990)

The USEPA's national dioxin survey also chose 2,4,5-trichlorophenol manufacturing and disposal sites as their 'Tier 1', ie those most likely to be contaminated with 2,3,7,8-TCDD (Fiedler *et al* 1990). Tier 2 consisted of sites associated with the manufacture and disposal of 2,4,5-trichlorophenol-derived pesticides, including 2,4,5-T. Within these two tiers, 99 sites were identified and 17 placed on the Superfund National Priority List (Fiedler *et al* 1990).

Published data in other countries confirm the prioritization of manufacture and disposal of chlorophenols, chlorophenoxy herbicides and associated process wastes as they are responsible for some of the highest recorded PCDD/F pollution levels. The site of the Spolana Chemical Company in Czechoslovakia is one of the most highly contaminated in the world despite the fact that production of chlorophenols occurred for only three years between 1965 and 1968. Production ceased because workers in the plant exhibited chloracne. Concentrations of between 0.6 and 2000 ng/g (ppb) of 2,3,7,8-TCDD were detected in production wastes; soil levels were up to 24 ug/g (ppm) 2,3,7,8-TCDD. Despite the low water solubility of PCDD/Fs, contamination was such that concentrations in groundwaters of 5 ng/L were recorded (Zemek and Kocan 1991).

In addition, metallurgical processes such as magnesium and nickel smelting have been found to produce PCDD/F

(Oehme *et al* 1989). PCDD/Fs can be produced from inorganic carbon and chlorine in high temperature systems. Favourable conditions such as the presence of catalysts (eg copper), alkaline conditions and phenolic compounds may lead to higher yields but are not essential. Indeed, in sewage sludge, highly chlorinated dioxins appear to be being produced from pentachlorophenol (Oberg *et al* 1992), showing that dioxin formation is not exclusively a high-temperature process, as had previously been widely thought.

Published data regarding on-site industrial contamination in the UK are almost non-existent. A level of 400 ppb 2,3,7,8-TCDD was recorded on the Coalite Chemicals site near Bolsover in Derbyshire after a chlorophenol accident in 1968 (Hutzinger *et al* 1982), but no recent on-site data are available despite the fact that chlorophenols and their derivatives, though not 2,4,5-T, continue to be manufactured (Anon 1991; Berryman *et al* 1991). In contrast, research is available on soil surrounding the facility (MAFF 1992a; MAFF 1992b; MAFF 1992c). In the absence of legislation on soil dioxin levels, regulatory authorities have focused much of their attention on stack emissions (Berryman *et al* 1991). However, gross soil contamination most frequently derives from spillage of highly concentrated products or residues, as illustrated by Table 2. The dioxin emissions from the stacks of hazardous waste incinerators are widely distributed, but high localized levels have been found, probably due to storage or spillage of wastes (Ball *et al* 1993). An unfortunate consequence of the lack of specific regulations or guidelines to protect soils from contamination, however, is that during investigations of soils (MAFF 1992a; MAFF 1992b; Ball *et al* 1993) the emphasis remains on attempting to estimate

Table 2. Concentrations of 2,3,7,8-TCDD in soils

Location	Concentration (ppb 2,3,7,8-TCDD)
Rural England (HM Inspectorate of Pollution 1989)	<0.0005
After 2,4,5-T spraying (1lb/acre,100 ppb TCDD) (Hutzinger *et al* 1982)	0.0001
Near Manchester, UK (HM Inspectorate of Pollution 1989)	0.0064
CDC level for concern in soil (HM Inspectorate of Pollution 1989)	1.0
Elgin AFB, Florida (Agent Orange spill) (Hutzinger *et al* 1982)	1.5
Chemie Werk, Linz, Austria (2,4,5-T production) (Hutzinger *et al* 1982)	140
Elgin AFB, Florida (Agent Orange spill) (Hutzinger *et al* 1982)	170
Coalite, UK (trichlorophenol accident) (Hutzinger *et al* 1982)	400
Horse arena C (Missouri) (Waste oil application) (Hutzinger *et al* 1982)	540
Phillips Duphar, NL (trichlorophenol accident) (Hutzinger *et al* 1982)	10 000
Spolana, Czech. (trichlorophenol production) (Hutzinger *et al* 1982)	24 200
Horse arena A (Missouri)(Waste oil application) (Hutzinger *et al* 1982)	32 000

human health effects via general exposure or contamination of foodstuffs rather than identifying locations requiring remediation.

TOXICITY AND TOLERABLE DAILY INTAKES

The human toxicity of dioxins, controversial for many years (Van Strum and Merrell 1990), is being clarified. A wide range of effects have been established epidemiologically in humans (Fingerhut et al 1991a; Fingerhut et al 1991b; Jenkins 1991; Manz et al 1991), including cancers, immunological abnormalies, neurophysical and psychiatric central nervous system effects, reproductive effects and metabolic disorders. Recent research also supports the case that humans are in fact more sensitive to the dioxins than had previously been assumed (Lucier 1991).

The World Health Organization (WHO) has set a tolerable daily intake (TDI) for PCDD/Fs of 10 pg 2,3,7,8-TCDD/ kg body weight/day (World Health Organization 1990). This TDI was later endorsed by the UK Committee on the Toxicity of Chemicals in Food, Consumer Products and the Environment (COT) and has subsequently been used by MAFF in its calculations of acceptable levels in milk and other foodstuffs (MAFF 1992a). Unfortunately, these decisions were made before the publication of the disturbing toxicological research described above and so some of the assumptions on which the calculations were based can no longer be supported. Most importantly, the WHO assumed that 2,3,7,8-TCDD was not a human carcinogen.

In contrast, the USEPA has based its acceptable daily intake (ADI) on the results of a two-year toxicity test on rats and assuming an acceptable risk of one cancer in a million (Greenlee et al 1991). As a result the US ADI is 6 fg/kg/day, 1670 times lower than the UK TDI. Further concern must arise from the fact that cancer appears to be a less sensitive response than immune and reproductive effects. In this light the WHO and UK tolerable daily intakes should urgently be revised.

HUMAN EXPOSURE VIA CONTAMINATED SOIL

Uptake from soil is generally regarded as minor compared with exposure via food. However, PCDD/Fs can be absorbed via the skin, lungs and gastrointestinal tract (Diliberto et al 1992).

There are no mandatory levels at which soil remediation should commence, but the USEPA has generally used a limit of 1 ppb 2,3,7,8-TCDD based on a risk assessment by the Centers for Disease Control (CDC) in Atlanta (Kissel and McAvoy 1989). This assessment has been supported by modelling of dermal absorption using fugacity-based calculations (Kissel and McAvoy 1989). Assuming 1 mg of soil per cm^2 of skin over 4% of the body surface (equivalent to both hands), it is predicted that over 4 hours 14.2% of the 2,3,7,8-TCDD would be absorbed, and over 8 hours, 26%. If the soil contained 1 ppb 2,3,7,8-TCDD, intake at this level would increase the body burden by 0.19 ng over 8 hours.

This represents almost one-third of the UK TDI. Intake at this level is of the same order as average daily dietary intakes which are variously calculated as 0.125 ng for the UK, 0.2 ng for Germany and 0.09 ng for Canada (MAFF 1992d).

The model also predicts that absorption rates remain the same as the dioxin concentration increases. Thus eight hours' exposure to soil at 100 ppb increases the body burden by 19 ng – far in excess of both the TDI and estimated food intake. Children playing are likely to be both more heavily exposed than adults, an important consideration when setting levels for remediation of residential sites. These calculations indicate that the CDC's 1 ppb 2,3,7,8-TCDD (or 2,3,7,8-TCDD equivalents) clean-up threshold for soil is far from conservative.

Of course, direct contact with contaminated soil is not the only human exposure route. Milk and dairy products are the largest contributors of PCDD/Fs in the average diet. Ingestion of contaminated soil by cattle accounts for between 20% and 29% of intake under normal conditions. (Travis and Hattemer-Frey 1991), the rest being accounted for by contamination of grain and herbage. Dioxins can volatilize from soil and become concentrated on plant leaves (Bacci et al 1992). Thus, where the soil itself is the source of contamination the proportion due to soil ingestion will inevitably be higher, although there will be a concomitant increase in the transfer from soil to plant surfaces by volatilization and deposition. Soil contamination levels far lower than 1 ppb also appear to be sufficient to cause unacceptable contamination of milk. In Derbyshire in April 1991, significant PCDD/F contamination of milk was discovered. Three farms near Bolsover were worst affected (MAFF 1992a). Two farms (A and C) produced milk for human consumption and the Milk Marketing Board declined to accept the milk since it contained concentrations of 1.8 and 1.9 ng TEQ/kg, which exceeded the MAFF Maximum Tolerable Concentration (MTC) of 0.7ng TEQ/kg. The third farm (farm B) did not supply milk but the beef herd was so affected that an order restricting its movement was obtained by MAFF under the Food and Environment Protection Act (MAFF 1992c).

The highest levels of dioxins recorded on farm A were 44 ppt in soil, 45 ppt in turf and 14 ppt in herbage. Maximum soil concentration on farm B was 54 ppt; no herbage was analysed. Maxima for farm C were 22 ppt in soil and 8.8 ppt in thistle (MAFF 1992e). The results suggest that land used in dairy production is particularly sensitive to contamination and measures need to be taken to ensure its protection.

INCREASES IN GENERAL PCDD/F SOIL CONTAMINATION

It is likely that most of the farm contamination near Bolsover derived from nearby chlorophenol and chloroaromatic manufacture. The volatilization of PCDD/Fs causes industrial sites to act as point sources to the wider environment. A nationwide survey investigated 'background' levels throughout the UK and showed elevated levels in urban areas and industrial regions (HM Inspectorate of Pollution 1989). Urban contamination is due to both industrial discharges and to diffuse

emissions, such as municipal incinerators and vehicles burning diesel or leaded petrol. In such areas, PCDD/Fs have been derived from a variety of sources, past and present. Significantly, though, two of the highest elevated levels recorded in the report were encountered in rural mid Wales and the border regions, and are probably due to a single local point source. Undoubtedly there are many such sources in rural areas, including numerous decommissioned factories or old dumpsites, but the scale of the problem is probably greatly underestimated. Local authorities, even if aware of the existence of historically damaged sites, might not suspect dioxin contamination and with analysis of a single sample costing between £700 and £1000, will often be precluded from undertaking extensive investigations.

Generalized contamination is, therefore, ubiquitous and furthermore, background levels are steadily increasing as a result of atmospheric deposition. The situation in the UK was investigated by Kjeller et al (1991) who analysed soils stored at intervals from the 1840s to the present. The plot sampled comprises part of the Rothamsted Experimental Station and had never been chemically treated. Increases in the concentrations of PCDD/Fs were seen just prior to the turn of the century; in total, concentrations approximately trebled over the studied period. This increase is concomitant with the manufacture and use of chlorinated hydrocarbons and the authors conclude the observed soil concentrations equate to an annual deposition rate of approximately 190 ng/m^2.

SITE REMEDIATION STRATEGIES: PAST AND FUTURE

Thus to protect human health, food purity, land values and prevent the further generalized contamination of the wider environment, it is vital that highly contaminated sites be cleaned up. This is both difficult and expensive and in the past the only frequently applied remediation methods were bioremediation and incineration; at other sites contaminated soil was capped, containerized or solidified; methods which served only to restrict migration of the PCDD/Fs without actually destroying them.

Bioremediation is unlikely to be successful because of the stability and toxicity of the group. Laboratory studies of biodegradation may be superficially attractive but offer only a very limited utility in practice. Such studies usually only monitor the disappearance of a single model compound from the culture without fully identifying degradation products (Hammel et al 1986). Hence a specific congener may only be partially degraded, or be converted to a closely related structure with high toxicity. Further, dioxins will not be the sole contaminants at any site; toxicity of co-contaminants will further inhibit microorganisms.

Incineration of contaminated soil, though widely practised, is particularly unsuitable because of the cost of treating large volumes and because it leaves a large residue of soil ash still to be disposed of. Destroyed topsoil will also have to be replaced at great expense if the site is to be fully regenerated.

When treating large quantities of soil with comparatively low levels of pollutants, it is naturally preferable to choose a method that either does not destroy the soil matrix (eg biodegradation) or to extract the contaminants. Solvent washing of soil has been used with some success but inevitably results in the release of large volumes of the solvent which may be toxic or flammable. Steam stripping is effective for the more volatile pollutants but less so for PCDD/Fs. The emerging technology of supercritical fluid extraction (SFE) is potentially far more effective than either of these methods. Supercritical processes involve the use of a compound at such temperatures and pressures that it simultaneously exhibits the properties of a liquid and a gas. Supercritical fluids are extremely effective solvents. They have found industrial applications in separating petroleum compounds and decaffeinating coffee, and laboratory use for sample extraction (Jain 1993; Newman 1993). SFE is most commonly carried out with carbon dioxide, which becomes supercritical above 31°C and 74 bars. Pilot-scale experiments in the USA have been successfully carried out on up to 5 kg of soil. The soil would be extracted with supercritical CO_2 and on subsequent reduction of temperature and pressure, the CO_2 evaporates, leaving only the contaminant residue. The CO_2 would be recycled, so no emissions would be necessary and no further waste produced. Non-toxic and non-combustible, CO_2 also has obvious safety and environmental advantages over the organic solvents previously used. The concentrated wastes derived from extraction processes would remain to be destroyed. Again, incineration has been regarded as a method of choice but is coming under ever closer scrutiny as a suitable waste disposal technology. It is itself a source of environmental PCDD/F contamination (Ball et al 1993) and the increasingly stringent emissions controls being imposed are becoming harder and harder to meet (see eg Carnes 1989). As an open-ended process necessarily emitting large volumes of effluents in gaseous and liquid phases, when concentrations exceed allowable limits there is no way to retain them for further treatment; they are unavoidably released into the environment (Wendt et al 1990). Even where compliance is achieved, it is frequently by the improved sequestering of PCDD/Fs by pollution control devices creating a further residue to be dealt with (Buonicore 1989). Incinerator residues are typically landfilled, creating a second generation of potentially hazardous land areas.

Closed-loop remediation technologies for a wide range of applications are becoming available (Picardi et al 1991). These include biological, chemical, electrochemical, and photochemical techniques, suited to different pollutants in different media and are at varying stages of development from the laboratory to production (Jain 1993; Picardi et al 1991). Biological methods, as discussed above, are not currently applicable to dioxin destruction. Dechlorination reactions, while potentially very effective in some applications, would in this case leave a toxic organic residue. It is also possible that highly chlorinated dioxins could actually increase in toxicity during treatment if they are converted to (for example) 2,3,7,8-TCDD. Physicochemical, chemical and electrochemical techniques which are capable of totally

destroying the molecule appear to have the most potential for dealing with PCDD/Fs.

However, while remediation of contaminated soils is vital to remove historical burdens that threaten human and environmental health, in the long run, the most cost effective solution is prevention. Although the UK government has made no commitment to soil clean-up, it has signed two significant pieces of international legislation regarding marine pollution. In 1990, it agreed to reduce by 70% inputs of PCDD/Fs to the North Sea (MINDEC 1990). In 1992 it signed the Paris Convention, thereby agreeing to reduce, with the aim of total elimination, toxic, persistent and bioaccumulative compounds, in particular organohalogen compounds. To achieve this a twofold approach will need to be taken. Firstly, processes acting as major current sources of PCDD/Fs should cease to be permitted and substitutes found for products known to be contaminated. However, this alone would not be enough. To prevent the continued diffusion of dioxin from historically contaminated sites, these must also be identified and cleaned up. If this policy is carried out it will not only reduce pollution of our surrounding seas but be of considerable benefit to the terrestrial environment.

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