Accumulation of Organochlorine Compounds in Agricultural Food Chains

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Introduction: Man - The End of the Chain

The combined properties of environmental persistence and mammalian toxicity displayed by many organochlorines make them pollutants of particular concern. The lipophilic compounds in particular (eg. polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/F), polychlorinated biphenyls (PCBs) and organochlorine pesticides) display a strong tendency to accumulate in human tissue. The ubiquity of these substances makes for a multitude of complex human exposure routes. An understanding of these environmental pathways to man is a prerequisite for developing strategies to reduce human exposure and for predicting the behaviour of other compounds.

The First Link: Dairy Products - Major Source of Human Exposure

The first step in a pathways assessment is to determine the primary direct sources of human exposure. Several studies of this question have been conducted, three of which are summarized in Table 1. Food, primarily animal fat, is seen to be primarily responsible for the PCDD/F and PCB burden. Indeed, one food group - dairy products - predominates, contributing about 50% of the daily PCDD/F dosage and 28% of the PCB dosage. This arises from the lipophilic nature of the contaminants and the dominant role of milk fat in the typical person's diet. While these figures represent the "average individual" and other sources such as fish could play a more dominant role in specific sub-groups, accumulation in agricultural food chains, and especially in cow's milk, is the critical exposure pathway for the general population to many organochlorines.

TABLE 1: Sources of Human Exposure to Organochlorines

Compound	Percent of Total Exposure					Source
	Fish	Milk	Meat	Eggs	Plants	
PCDD/F	15	45	23	16	1	Environment Ontario, 1988
PCDD/F	29	56	8	1	6	Beck et al., 1987.
PCB	34	28	21	3	14	Sümmermann et al., 1978

The Second Link: The Cow - A Contaminant Pipeline

Milk cows have been the subject of numerous feeding studies in which the animals were fed contaminated feed (Fries, 1977; Tuinstra et al., 1981; Jensen and Hummel, 1982; Firestone et al, 1979). Various authors used these data to define carryover factors, the ratio of the milk to the feed concentrations (Travis et al., 1988; Heeschen and Blüthgen, 1985; Connett and Webster, 1987). In a recent study of a cow under natural conditions we took a different approach, showing that virtually all of the persistent contaminant that finds its way into the cow is excreted in the milk (McLachlan et al., 1990; McLachlan and Hutzinger, 1990a). Hence a cow can be understood as a pipeline: inflow = outflow.

The problem is knowing which compounds are persistent. At the moment one is dependent on experimental evidence. For instance, we know that the 2,3,7,8-substituted PCDD/F isomers are persistent while the other PCDD/F are not. Similarly, it has recently been suggested that the 2,4,4' substitution pattern is the key to PCB persistence in the cow (McLachlan and Hutzinger, 1990a). However, the lack of predictive methods for chemical persistence remains a major handicap in modeling contaminant behaviour in the cow.

The ability of a cow to degrade a substance does not preclude its appearance in the milk. Indeed, a small fraction of the uptake of labile PCDD/F and PCBs is excreted in milk (McLachlan and Hutzinger, 1990a). This "short-circuited" fraction was observed to increase with increasing lipophilicity of the compound (from 2% to 11% for PCBs). It is not clear whether this is due to a physico-chemical phenomena or slower degradation kinetics for the more chlorinated isomers.

The cow has a second pathway besides milk to rid itself of contaminant, namely the feces. Our cow mass balance showed that the lactating animal also excreted some resorbed contaminant by this route. However, it was generally much less significant, ranging from 0% to 15% of excretion by milk. In beef cattle feces represent the only significant possibility to excrete ingested persistent contaminants. As this route is much less favourable than lactation, tissue concentrations will likely be determined by the ratio of ingestion to growth dilution.

A cow need not always be in a steady state characterized by the relationship: input=output. Changes in the feed contaminant level or the dry period prior to calving when the cow gives no milk but gains weight (typically 6 weeks) can upset the balance, and the cow's body requires time to adjust to the change. Feeding studies have shown clearance half lives of about 1.5 months for a wide range of lipophilic substances (Fries, 1977; Jensen and Hummel, 1982). Our measurements of milk of the first milk pproduced by a young cow give similar results (Figure 1). These observations can be interpreted as the buffering effect of the cows body fat. A 600 kg cow with 6% body fat producing 1.2 kg of milk fat a day excretes its body fat weight in milk fat once every 30 days.

FIGURE 1
1,2,3,7,8-Cl5DD Concentration in Cow's
Milk Immediately After the First Calf

The Third Link: Leafy Plants - Pollutant Accumulators

How do these pollutants get into the cow? Modeling studies have concluded that feed is responsible for the bulk of the cow's exposure (Stevens and Gerbec, 1988). These results were confirmed by our contaminant mass balance of a cow, which showed that feed accounts for virtually 100% of the uptake (McLachlan et al., 1990; McLachlan and Hutzinger, 1990a).

Soil has also been suggested as a source of contaminant, particularly for pasturing cows. In a review of soil consumption by cattle, Fries (1987) reported that soil comprised between 1% and 18% of the dry weight eaten by pasturing animals, depending on the supply of grass, and that offering supplementry feed reduced the soil consumption by more than half. For cattle that were on the pasture 12 months of the year, the average value was 6%. In Bayreuth the cows are on the pasture 6 months of the year, the grass supply is always abundant, and they receive supplementry feed. A soil consumption of 1-2% of the dry matter uptake would appear to be a realistic estimate in this situation.

Using PCDD/F as an example, the average feed concentration in Bayreuth was 0.44 pg TE/g DW (International toxic equivalents per gram dry weight). The soil concentration in a field in the area was 0.8 pg TE/g DW. Thus soil could account for 2-4% of the cow's PCDD/F uptake in this case. This was confirmed by following the milk concentrations of a cow during the transition from barn to pasture feeding. As seen in Figure 2, the milk concentrations actually decreased when the cow was put out to pasture.

If the soil concentration was 22-44 pg TE/g DW, the contaminant load from soil would equal that from feed. Soil concentrations of this magnitude have been reported close to industrial areas. In such cases it might be appropriate to investigate whether the animal husbandry practices employed in these areas lead to elevated contaminant levels in milk.
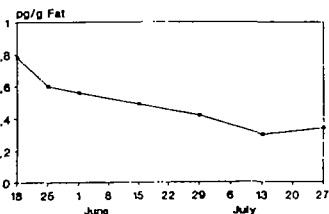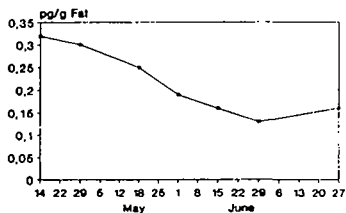

FIGURE 2
1,2,3,7,8-Cl5DD Concentration in Milk
Pasture Feeding Began on May 5

Not all of the contaminant ingested by a cow is resorbed in the digestive tract. Our mass balance studies indicated that the resorption decreases with increasing lipophilicity (see Figure 3). While it is above 80% for log 1-octanol-water partition coefficients ($logK_{ow}$) values up to 6.5, the resorption then falls off quickly, reaching 23% for Cl_8DD. It is not known if the resorption is significantly different for different feed types. Resorption from soil for instance might be lower than from grass.

The contributions of the different feed types to the exposure to three contaminants at our study farm are shown in Figure 4. The grass products, namely the different hay cuts and the grass silage, account for the majority of the load, while corn silage plays a secondary role. Grain is a negligible pollutant source.

This has implications for feeding practices. All cows have a basic dietary requirement of grass which brings a milk production of about 12 L/d. The production can be increased to 35 L/d and more by feeding grain. Therefore, a cow on a high grain ration would produce twice as much milk with the same contaminant content as a cow on a low grain ration, ie. milk with half the contaminant concentration.

In Figure 5 the dry weight concentrations of PCB 153 in corn leaves, corn silage (leaves, stalk and cobs), hay and grain are plotted. The leaves, which have the highest surface area/weight ratio, clearly accumulate much more contaminant than the whole plant or just the grain. Leafy plants are the major source of organochlorines for the cow, and hence for the milk.

FIGURE 3
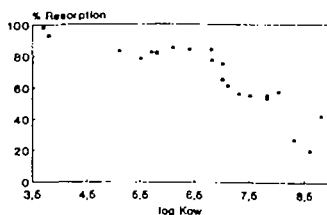Digestive Tract Resorption in Cow
vs log Kow

FIGURE 4
Contribution of Different Feeds
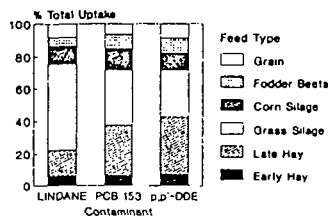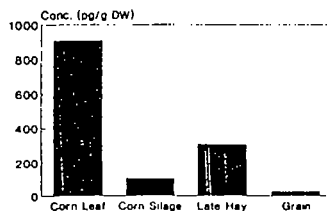to the Cow's Contaminant Uptake

FIGURE 5
PCB 153 Concentrations in
Different Plant Material

The Fourth Link: Air - Gas Phase Diffusion or Particulate Deposition?

There are two basic ways for pollutants to reach plant leaves: through the soil, roots and stem; or through the air. Although soil uptake was long the subject of scientific investigation, Bacci and Gaggi (1985) demonstrated in an elegant experiment that root uptake of PCBs is insignificant in comparison to the pathway soil-air-plant. This is likely also the case for the PCDD/F, which have lower water solubilities and are thus even less mobile in the plant's aqueous transport media. Organochlorines with a high water solubility and relatively low lipophilicity such as lindane may be exceptions to the generalization that root uptake and plant translocation is an insignificant pathway for this class of compounds

The role that the soil-air-plant transfer observed by Bacci plays in the real world has not yet been extensively investigated for organochlorines. Studies with another family of compounds, the PAHs, have shown that plants growing on extensively contaminated soils do not have significantly higher levels than plants growing on uncontaminated soils (Kampe, 1987). This indicates that the substance diffusing out of the soil is quickly diluted by the air in the plant canopy, so that the plants see an air concentration very close to the ambient level

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Organohalogen Compounds 1   481

Another possible route to the leaf is direct application. As the use of organochlorine compounds in West Germany has largely been forbidden, the major remaining form of direct deposition is through the spreading of sewage sludge. It has been demonstrated that heavy metals in sludge adhere to forage following spraying, and that they are not completely washed off by heavy rain (Chaney and Lloyd, 1979). Organochlorines could also accumulate on plants following direct application of sewage sludge. Organic contaminants in sewage sludge have been shown to accumulate in soil (König et al, 1987; Kampe, 1987; McLachlan and Reissinger, 1990), which once again raises the question of soil ingestion by grazing cattle. As these issues have yet to be satisfactorily resolved, the application of sewage sludge on forage has been forbidden in West Germany.

By the process of elimination the accumulation of organochlorines in plant leafy parts must be due to aerial deposition. There are three possible mechanisms: wet deposition, dry particulate deposition, and dry gaseous deposition.

Rain and snow can capture large quantities of gaseous and particle bound matter on its descent to the earth, resulting in high fluxes to receiving surfaces. The gas phase stripping of relatively insoluble compounds such as PCBs is much less effective than the particle scavenging (Duinker and Bouchertall, 1989). On the other hand, the annual wet deposition of these compounds is five to ten times less than the dry particulate deposition (Hites, 1990), so that the latter can be expected to be more important. In addition, rain washes off contaminants already present on the leaves. Therefore, wet deposition is likely not a significant pathway of lipophilic organochlorines to plant surfaces, with the possible exception of very soluble compounds such as lindane.

Particle deposition has commonly been assumed to be responsible for the transport of involatile organochlorines such as PCDD/F to plant surfaces (Stevens and Gerbec, 1988; McKone and Ryan, 1989). However, recent studies have demonstrated that plants absorb significant quantities of these compounds out of the gas phase (Bacci et al., 1990; Reischl et al., 1989). Moreover, our measurements of organochlorines in the air during the growing season showed that over 95% of the PCBs up to a chlorine number of 6 and a large fraction of the PCDD/F were present in the gas phase (McLachlan and Hutzinger, 1990b).

We attempted to evaluate the significance of these two processes using the air and plant data collected during the same growing season in Bayreuth. We first assumed that the Cl_8DD and Cl_8DF measured in the plants were tracers for particle deposition. The particle bound component of the other PCDD/F in the plant was then estimated by scaling the PCDD/F particulate data. The results are plotted in Figure 6. Particle deposition could account for the Cl_7DD/F in corn leaves, but would appear to make a minor contribution to the Cl_4DD/F accumulation. This suggests that gas phase diffusion of the lower chlorinated PCDD/F homologues to the leaves plays an important role in plant uptake.

It has been suggested by several authors that gas phase transport of contaminants to plants is a partitioning process that should correlate with the 1-octanol-air partition coefficient K_{oa}, just as sediment-water partition coefficients correlate with K_{ow} (McLachlan et al., 1989; Mackay and Paterson, 1989; Bacci et al., 1990) In Figure 7 the ratios of the non-particle bound corn leaf concentration to the gas phase concentration (on a volume/volume basis) are plotted against K_{oa} for organochlorines ranging from tetrachlorobenzene (TCB) to Cl_6DD. The correlation is much flatter than the linear relation predicted. Whereas the leaves behave as if they had a higher solubility for TCB than 1-octanol, they would appear to have less than 1/5000 of the 1-octanol solubility for Cl_6DD.

FIGURE 6
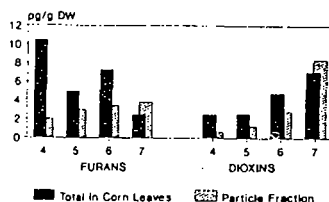Comparison of PCDD/F in Corn Leaves and the Fraction Attributed to Particles
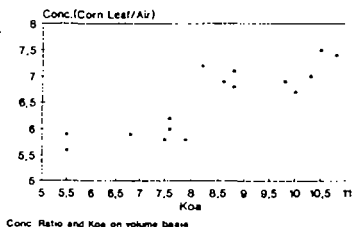
■ Total in Corn Leaves   ▨ Particle Fraction

FIGURE 7
Plot of Corn Leaf/Air Gas Phase Concentration Ratio vs Koa

Conc. Ratio and Koa on volume basis

The reason for this observation may lie in the kinetics of gaseous contaminant uptake by the plant. Organochlorine clearance half lives in the order of months have been found for spruce needles, with estimated times to reach equilibrium in the years (Reischl et al., 1989). Thus agricultural crops may never achieve equilibrium with the surrounding air. The practical consequence: Fast growing versions of the same crop are likely less contaminated. The impractical consequence: Modelling chemical fate in agricultural food chains becomes more difficult, as non-equilibrium considerations as well as growth dilution must be considered.

The Final Link: The Sources - Old and New

Where do the contaminants in the air come from? One source for many compounds is continuing emissions. PCDD/F for instance continue to be released by automobiles and various combustion processes. Many organochlorine compounds are no longer in use however, but are nevertheless still present in the air. A good example, PCBs in the USA, has been extensively documented by Manchester-Neeswig and Andren (1989). They postulate that the earth is acting as a PCB reservoir in a dynamic quasi-equilibrium with the atmosphere. Thus, as long as PCBs are present on the earth they will also be found in the air.

This has significant implications for future efforts to reduce food chain exposure to lipophilic organochlorines. It is clear that air concentrations must be reduced to interupt the food chain accumulation of these substances. However, reducing emissions will not necessarily lead to an immediate reduction in air levels. Rather, the decrease will depend on the response of the complete ecosystem to the reduced emissions. Of particular importance is the existing equilibrium discrepency between the earth's surface and the atmosphere, and the rate at which contaminant is removed from the interactive environment. While there is some knowledge about the response of aquatic ecosystems, very little information is available about terrestrial ecosystems.

Summary

The dominant route of human exposure to many lipophilic organochlorine contaminants begins with atmospheric emissions, both directly through sources and indirectly through release of accumulated substance from the terrestrial and aquatic environments. These compounds in the air are deposited on plant surfaces, to a large degree through gaseous diffusion. The plants are ingested by cows, and most of the contaminant is resorbed in the animal's digestive tract. Many compounds are degraded in the animal, but those that are persistent are excreted almost quantitatively in the milk. Man consumes large quantities of milk products, resulting in significant exposure to organochlorines.

The Weak Links: Research Needs

Contaminant behaviour in the cow is relatively well understood. Further study of other livestock such as pigs, chickens or beef cattle would be useful, but the big deficit in this area remains the lack of predictive models for degradation in the animal.

There is continuing uncertainty as to the effect of sewage sludge fertilization and contaminated soils on food chain accumulation. While these are regional issues of considerable economic significance that warrant further investigation, the dominant route for most organochlorines into the food chain is through grass.

The most significant gap in our knowledge is the air-plant interface. The issue of how organochlorine compounds in the air are transfered to plant surfaces has not yet been satisfactorally resolved, and the questions such as species differences, degradation on and in plants, kinetics and temperature dependence have hardly been addressed.

Finally, the reaction of the complete ecosystem to changes in emissions needs to be studied.

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