# THE EFFECTS OF RIVER FLOODING ON THE CONGENER PATTERNS OF DIOXINS IN SOIL, HERBAGE, AND COWS' MILK FROM FLOOD-PRONE FARMS

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## Introduction

Cows'milk from farms in urban or industrial areas generally contains higher levels of dioxins and PCBs than milk produced in rural areas. This is generally attributable to atmospheric deposition to herbage and soil where cows graze. However, contamination of pasture as a consequence of the deposition of sediment due to flooding of rivers that flow through urban and industrial areas can lead to increased levels of dioxins and PCBs in pasture. The first evidence for this was a small-scale study which showed higher levels of dioxins in cows' milk and soil from the River Rhine flood plain compared with background values.[1] The long-term effects of flooding on the levels of dioxins and PCBs in milk, soil and herbage from flood-prone and non-flooding dairy farms has now also been investigated in greater depth in a controlled study using matched flood-prone and nearby non-flooding farms along three river systems in the UK.[2,3] Multivariate regression showed that the ΣWHO-TEQ for dioxins and dioxin-like PCBs and the ΣICES7 PCB concentrations were significantly higher in milk from flood-prone farms than for milk from matched control farms along the River Trent and along the Doe Lea / Rother / Don river system. However, in contrast to these rivers that flow through urban industrial areas, milk from flood-prone farms along the rural River Dee, did not contain higher ΣWHO-TEQ and ΣICES7 PCB levels than milk from the corresponding control farms.[3] Elevated ΣWHO-TEQ values were also found in soil from flood-prone rivers along the Trent and the Doe Lea / Rother / Don river systems.[3]

Analysis of the dioxin congener patterns in cows' milk, air and contaminated river sediment has also been used to investigate the cause of the elevated levels of dioxins found in cows' milk from a farm next to the River Rother that is frequently affected by floodwater from the river.[4] The congener profiles for dioxins in the milk from the flood-prone farm and a nearby control farm were shown to be distinct. Furthermore, the congener profile of the milk from the flood-prone farm was shown to be similar to that of the sediment in the River Rother, which contains unusually high levels of 2,3,7,8-TCDD, suggesting that the high levels of dioxins in milk from the affected farm are likely to be due to the cumulative effects of deposition of contaminated river sediment onto the pasture. However, the study by Alcock *et al* lacked data on dioxin levels in soil and herbage at the flood-prone farm itself but instead utilised data for sediment from the River Rother at a site about 7 km upstream of the farm that had been published previously.[4,5]

## Materials and Methods

The data presented here were collected as part of a large controlled investigation into the effects of flooding on the levels of dioxins and PCBs in cows' milk, soil and grass, which was conducted for the Food Standards Agency, UK. The overall study design, sampling and chemical analyses have been described in detail previously.[2,3] Very briefly, dairy farms where pasture is periodically inundated with floodwater were selected at sites along each of the three river systems investigated. Control farms that are not subject to flooding, but which are close to each of the flood-prone farms were also selected so that each pair of farms would be expected to experience similar levels of atmospheric deposition of dioxins and PCBs. The milk, soil and herbage samples discussed in this paper were collected in October 1998 and August 1999. The bioconcentration model developed by Lorber *et al*, which incorporates congener-specific bioconcentration factors (BCFs) for the transfer of individual dioxin congeners from feed to milk fat, that were calculated by McLachlan *et al*, can be used to predict dioxin concentrations in milk.[6,7] A simplified version of this model was used to estimate the likely congener profile (but the not the absolute concentration) of dioxins in milk from cows grazing solely on flood-prone or non-flooding sites on Farms 9 and 13. Very briefly, the dioxin concentration in grass was multiplied by the corresponding BCF value for each congener to generate the potential congener profile in milk from cows grazing on that grass. Results for Farm 9, using this method, are shown in Figure 1.

**Results and Discussion**
As shown in Table 1, the total concentrations of dioxins in the milk samples collected from two flood-prone farms, located next to the Rivers Rother and Don, were much higher than in the corresponding milk samples collected from the nearby matched control farms. In October 1998, soil and herbage samples were collected from two sites on each of these flood-prone farms. For Farm 13, one set of grass and soil samples was collected from the side of the levee that regularly becomes inundated with flood-water, and the other set was from the far side of the levee, which is protected from flooding. In the case of Farm 9, the non-flooding samples of soil and herbage were collected from non-flooding high ground some 50 metres from a flood-prone site from which the other samples were collected. As shown in Table 2, both the soil and herbage samples from flood-prone sites contained much higher concentrations of dioxins than at the matched non-flooding sites. Table 2 also shows that the dioxin concentrations in soil and herbage samples collected from control farms 10 and 12 were much lower than those in the corresponding samples collected from the flood-prone sites on farms 9 and 13.

**Table 1. Concentration of dioxins in milk samples from matched pairs of flood-prone and control farms (ng WHO-TEQ/kg fat)**

| Sampling date | Farm 9 | Farm 10 | Farm 13 | Farm 12 |
|---|---|---|---|---|
| Oct-98 | 5.96 | 1.03 | 4.26 | 0.68 |
| Aug-99 | 4.37 | 0.96 | 0.75 | 0.68 |

**Table 2. Concentration of dioxins in soil and herbage samples (ng-WHO-TEQ/kg dry wt)**

| | Farm 9 (flood-prone) | | Farm 10 | Farm 13 (flood-prone) | | Farm 12 |
|---|---|---|---|---|---|---|
| | Flood-prone | Non-flooding | (Control) | Flood-prone | Non-flooding | (Control) |
| Soil | | | | | | |
| Oct-98 | 537 | 21.6 | - | 38.4 | 5.25 | - |
| Aug-99 | 741 | - | 10.5 | 34.0 | - | 6.43 |
| Herbage | | | | | | |
| Oct-98 | 3.09 | 0.84 | - | 2.62 | 0.46 | - |
| Aug-99 | 0.99 | - | 0.15 | 0.14 | - | - |

Analysis of sediment samples from the River Rother has indicated that it has a very characteristic dioxin congener profile.[5] This congener profile has been reported to be distinct from the likely contemporary congener profile for ambient air in the area and from typical background soil dioxin congener patterns.[4] Based on the relatively limited available data, the sediment from the River Rother contains an unusually high proportion of 2,3,7,8-TCDD, compared with other environmental media, and correspondingly low proportions of other congeners, especially 1,2,3,7,8-PeCDD and 2,3,4,7,8-PeCDF, that normally contribute most to the Σ WHO-TEQ.

The flood-prone dairy farm next to the River Rother that was investigated by Alcock *et al* (2002) was fortuitously the same as Farm 9 in the Food Standards Agency (FSA) study, which was included in the study because of its known history of flooding and previous evidence that milk from this farm contained high levels of dioxins.[4,8] Whereas data on dioxin concentrations in soil and herbage were not available for the study by Alcock *et al* (2002), the soil and herbage data from the flood-prone and non-flooding sites at Farms 9 and 13 in the FSA study does allow direct comparison between the dioxin congener profiles in these environmental media and the concentration in milk.

As shown in Table 3, 2,3,7,8-TCDD contributes more than 50% to the Σ WHO-TEQ in the milk from flood-prone Farm 9 for both the October 1998 and August 1999 samples. By contrast, for the corresponding milk samples from the matched non-flooding farm (Farm 10), 2,3,7,8-TCDD only contributed less than 13% to the Σ WHO-TEQ. Conversely, for 1,2,3,7,8-PeCDD and 2,3,4,7,8-PeCDF contributed about 30% and 40% respectively to the ΣWHO-TEQ in the milk samples from Farm 10, but only about 15% and 20-25% of the Σ

WHO-TEQ for the milk samples from Farm 9. Similarly, the HxCDFs also made a smaller contribution to the ΣWHO-TEQ for the milk samples from Farm 9 than for those from Farm 10. Similar, but less dramatic, differences between the congener profiles for soil and grass samples from flood-prone Farm 13 and control Farm 12 are also clearly apparent as shown in Table 3.

**Table 3. Congener profiles of dioxins in milk from flood-prone and matched control farms (% of total WHO-TEQ)**

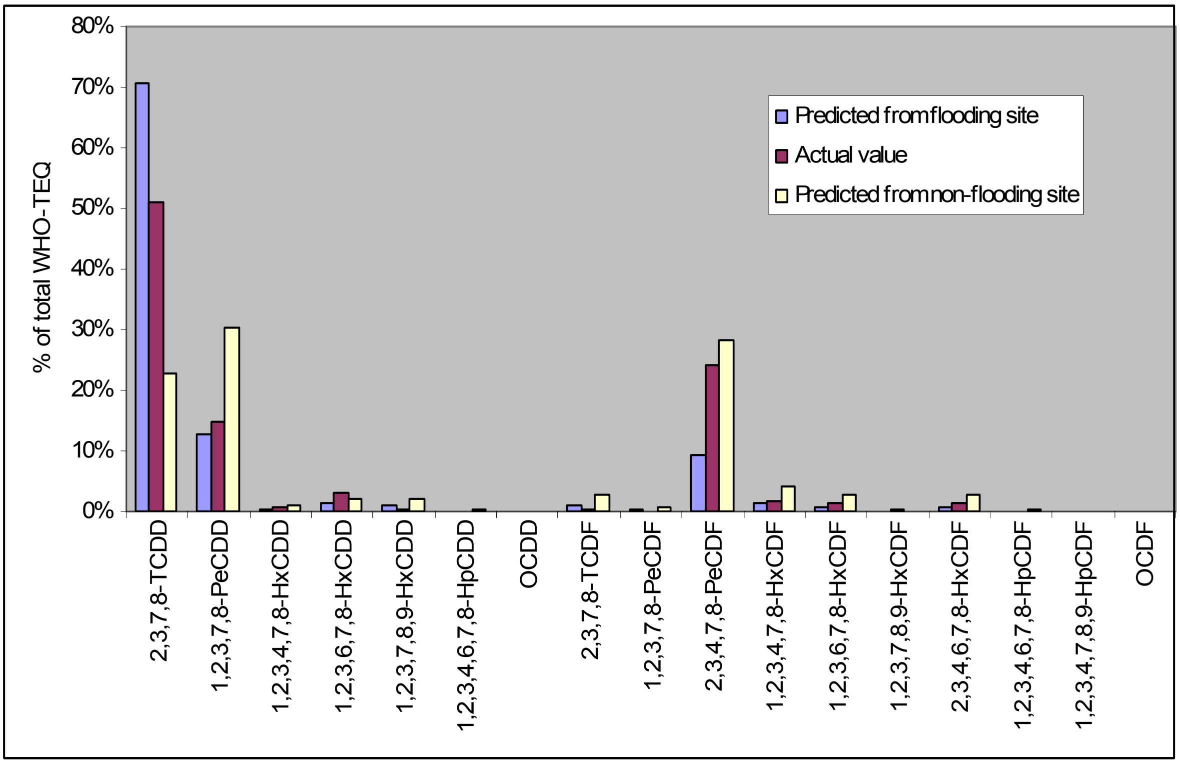
| | Farm 9 | | Farm 10 | | Farm 13 | | Farm 12 | |
|---|---|---|---|---|---|---|---|---|
| | Oct '98 | Aug '99 | Oct '98 | Aug '99 | Oct '98 | Aug '99 | Oct '98 | Aug '99 |
| 2378TCDD | 50.9% | 57.2% | 12.6% | 12.5% | 34.3% | 33. 5% | 16.1% | 17.7% |
| 12378PeCDD | 14.9% | 15.1% | 34.0% | 31.2% | 25.3% | 25.4% | 38.1% | 29.6% |
| 123478HxCDD | 0.60% | 0.41% | 1.26% | 1.56% | 1.20% | 0.94% | 1.61% | 1.33% |
| 123678HxCDD | 3.06% | 2.93% | 3.01% | 3.85% | 3.71% | 2.94% | 3.67% | 3.35% |
| 123789HxCDD | 0.49% | 0.82% | 1.36% | 1.35% | 1.15% | 0.94% | 2.79% | 1.33% |
| 1234678HpCDD | 0.15% | 0.09% | 0.20% | 0.34% | 0.26% | 0.21% | 0.31% | 0.31% |
| OCDD | 0.018% | 0.001% | 0.006% | 0.003% | 0.010% | 0.002% | 0.009% | 0.003% |
| 2378TCDF | 0.45% | 0.21% | 0.78% | 0.52% | 0.38% | 0.54% | 1.17% | 0.59% |
| 12378PeCDF | 0.15% | 0.069% | 0.34% | 0.16% | 0.22% | 0.13% | 0.44% | 0.15% |
| 23478PeCDF | 24.1% | 19.2% | 36.5% | 39.6% | 26.5% | 29.4% | 27.1% | 37.7% |
| 123478HxCDF | 1.86% | 1.63% | 3.21% | 3.02% | 2.65% | 2.41% | 2.93% | 2.81% |
| 123678HxCDF | 1.43% | 1.10% | 3.11% | 2.92% | 1.90% | 1.74% | 2.20% | 2.37% |
| 123789HxCDF | 0.27% | 0.023% | 0.97% | 0.10% | 0.40% | 0.13% | 1.47% | 0.15% |
| 234678HxCDF | 1.49% | 1.10% | 2.33% | 2.71% | 1.88% | 1.61% | 1.61% | 2.20% |
| 1234678HpCDF | 0.071% | 0.043% | 0.14% | 0.14% | 0.087% | 0.080% | 0.21% | 0.13% |
| 1234789HpCDF | 0.030% | 0.007% | 0.12% | 0.021% | 0.049% | 0.013% | 0.18% | 0.015% |
| OCDF | 0.022% | 0.0001% | 0.0024% | 0.0004% | 0.015% | 0.0005% | 0.0037% | 0.0006% |

**Table 4. Congener profiles in soil from flood prone and matched control farms (% of total WHO-TEQ)**

| | Farm 9 | | | Farm 10 | Farm 13 | | | Farm 12 |
|---|---|---|---|---|---|---|---|---|
| | Oct-98 | Aug-99 | Oct-98 | Aug-99 | Oct-98 | Aug-99 | Oct-98 | Aug-99 |
| | Flood | Flood | Non-flood | Non-flood | Flood | Flood | Non-Flood | Non-Flood |
| 2378TCDD | 78.1% | 83.8% | 15.6% | 8.49% | 45.2% | 39.2% | 10.3% | 7.31% |
| 12378PeCDD | 7.83% | 5.89% | 17.2% | 21.7% | 14.9% | 18.3% | 17.5% | 19.4% |
| 123478HxCDD | 0.16% | 0.13% | 1.69% | 2.26% | 0.65% | 0.75% | 1.62% | 1.71% |
| 123678HxCDD | 3.01% | 2.23% | 3.66% | 3.84% | 6.26% | 7.02% | 3.16% | 3.17% |
| 123789HxCDD | 2.22% | 1.72% | 3.05% | 3.65% | 4.94% | 5.30% | 2.63% | 2.80% |
| 1234678HpCDD | 0.50% | 0.47% | 3.62% | 3.30% | 2.82% | 2.56% | 3.73% | 3.06% |
| OCDD | 0.028% | 0.027% | 0.10% | 0.082% | 0.19% | 0.14% | 0.20% | 0.087% |
| 2378TCDF | 1.32% | 0.80% | 6.29% | 5.33% | 4.00% | 3.95% | 8.31% | 8.01% |
| 12378PeCDF | 0.39% | 0.24% | 2.18% | 2.47% | 1.05% | 1.21% | 2.57% | 2.71% |
| 23478PeCDF | 3.70% | 2.64% | 28.0% | 28.1% | 10.4% | 11.7% | 29.5% | 31.1% |
| 123478HxCDF | 1.22% | 0.95% | 6.26% | 6.23% | 3.73% | 3.92% | 7.19% | 6.89% |
| 123678HxCDF | 0.56% | 0.40% | 4.51% | 5.09% | 1.98% | 2.02% | 4.77% | 4.98% |
| 123789HxCDF | 0.059% | 0.038% | 0.20% | 0.43% | 0.20% | 0.18% | 0.50% | 0.36% |
| 234678HxCDF | 0.67% | 0.48% | 4.74% | 5.84% | 2.12% | 2.14% | 4.90% | 5.33% |
| 1234678HpCDF | 0.21% | 0.18% | 2.68% | 2.90% | 1.31% | 1.33% | 2.74% | 2.77% |
| 1234789HpCDF | 0.041% | 0.0014% | 0.19% | 0.25% | 0.16% | 0.18% | 0.26% | 0.24% |
| OCDF | 0.0037% | 0.0038% | 0.020% | 0.028% | 0.045% | 0.037% | 0.040% | 0.035% |

The congener profiles for soil samples from the flooding sites at Farms 9 and 13 would be expected to be influenced by the accumulation of contaminated river sediment following repeated inundations with floodwater over the years. Therefore it is not surprising that the soil congener profiles (shown in Table 4) for the flooding sites but not the non-flooding sites, resemble the characteristic congener profile of the river sediment that has been reported by Jones and Duarte-Davidson.[5] The herbage congener profiles (not shown) for the flooding and non-flood prone sites are similar to the corresponding soil congener profiles.

**Figure 1. Predicted and measured dioxin congener-profile in milk from Farm 9 in October 1998**




Due to uncertainties regarding the relative quantities of grass and soil ingested at flood-prone and non-flooding sites on Farms 9 and 13, quantitative predictions of dioxins in milk from cows reared on these farms were not attempted. However, congener profiles for milk from cows grazing solely on grass from flood-prone or non-flooding sites were estimated. Comparison between these predicted congener profiles and the corresponding measured congener profiles for milk from Farms 9 and 13 gives a strong indication that dioxins derived from the river sediment do contribute substantially to the overall dioxin content of the cows' milk from these farms. Figure 1 shows that the actual profile for milk is intermediate between the congener patterns that would be expected if cows were to graze entirely on non-flooding pasture or entirely on areas that flood at Farm 9. This is what would be expected assuming that the cows graze on both flood-prone and non-flooding areas of this farm.

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