DIOXINS FORMED DURING FIRES, A THREAT TO THE FOOD CHAIN?

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Introduction

Burning of certain materials like PVC-plastics, PCB-containing materials and certain pesticides is a well-known source of dioxins. This means that also incidental fires may result in the formation of dioxins, which may deposit at adjacent agricultural farm land[1,2]. This may cause increased exposure of food-producing animals and subsequently increased levels in animal-derived products for human consumption. In the EU, products exceeding the limits are not fit for consumption and can lead to the temporary closure of farms with huge financial impact. In the Netherlands a rapid emergency team, called BOT-mi and consisting of experts from various institutes, is involved in advising on the potential consequences of larger fires. Depending on the materials involved in the fire, additional samples of air, dust and grass are taken and investigated for dioxins, polyaromatic hydrocarbons and heavy metals. The present paper describes the outcome of a number of fires and their potential impact on the food chain.

Materials and methods

Samples of air, dust and grass were in most cases collected by the MOD (Environmental Incident Service), a mobile emergency team that is part of RIVM, at locations near the fire. Based on a first assessment and measurements in the smoke, it was decided whether samples should be analysed by RIKILT for dioxins and dl-PCBs. If so, grass samples were homogenized under liquid nitrogen and GC/HRMS analysis was carried out as described previously[3] based on the extraction with ASE and clean-up on a Powerprep system (FMS). Results are expressed in TEQ based on the application of the TEFs from 1998 which were applicable at that time according to EU-legislation[4]. According to the legislation, levels in grass used as feed should be expressed on 88% dry matter. The maximum levels for dioxins and the sum of dioxins and dl-PCBs in feed of plant origin were 0.75 and 1.25 ng TEQ/kg (until April 2012). In some cases also CALUX analysis was performed to investigate the potential use of the bioassay during incidents. The assay was carried out as described previously[5]. In short, samples were mixed with methanol/water and extracted with hexane/diiethylether and subsequently cleaned-up over an acid silica column. The eluate was evaporated, dissolved in a small amount of DMSO and mixed with the culture medium used to expose the 1.1 pGudLuc transfected H4IIE-cells.

Results and discussion

Cases

In the past years there were a number of fires where a substantial amount of grass samples were investigated just after the fires and a week or more later. The most important incidents are described below.

Coevorden

Half of May 2009, there was a fire at a company recycling old metals near the city of Coevorden. The smoke of the fire went over a number of farms with cows and goats (Figure 1). The day after the fire a number of grass samples were collected and analyzed for dioxins with GC/HRMS. A sample next to the fire (B) showed a dioxin level of 219 ng TEQ/kg, whereas a background sample taken from the other side of the fire (A) showed a level of 0.2 ng TEQ/kg. Levels of dl-PCBs at these two locations were 37 and 0.2 ng TEQ/kg. Samples taken at 0.2 (C), 0.3 (D), 0.5 (E), 0.6 (F) and 0.8 km west of the fire showed dioxin levels of 8.8, 4.5, 3.0, 3.0 and 2.2 ng TEQ/kg. The levels of dl-PCBs were lower at all locations but showed a relatively high contribution when compared to the level at site B. Levels of the 6 indicator-PCBs (ndl-PCBs) were also analysed and showed levels of 0.8, 35.3, 8.9, 4.9, 3.1, 2.4 and 1.5 µg/kg (for comparison, new EU-limit valid since April 2012 is 10 µg/kg).

As a precautionary measure, cows and goats were kept inside but during the fire farmers were harvesting the grass for the winter period. One sample was analysed and showed dioxin and dl-PCB levels of 3.1 and 1.1 ng TEQ/kg. This is one of the major concerns since such grass will be fed during a prolonged period, whereas grass in the pasture will continue to grow resulting in decreased levels.
One week after the fire, during which there was considerable rain fall, new samples were collected at locations C and G showing decreased dioxin levels of 1.8 and 0.5 ng TEQ/kg (about 50% decline). Strange enough, dl-PCB levels declined much less being respectively 2.8 and 0.8 ng TEQ/kg (20% decline) and being higher than the dioxin levels. This suggests either another source of the dl-PCBs, or, maybe more likely, a more rapid decline of dioxins compared to dl-PCBs. There was no other industrial activity close to this site. At both sites also soil samples were taken, showing dioxin and dl-PCB levels of 1.7 and 0.5 ng TEQ/kg dm at location C and 1.2 and 0.2 ng TEQ/kg dm at location F. The pattern in the soil samples was similar to that in the grass but the question is how specific this pattern is (see below).
Grass samples were also analysed with the CALUX-assay and showed a good correlation with the GC/HRMS data. The response measured at the various locations A to F was 58 (A), 5950 (B), 2226 (C), 1735 (D), 2181 (E), 1034 (F) and 765 (G) RLUs. This demonstrates that the bioassay can be used to make an inventory of the potentially affected area, allowing the analysis of 20-40 samples within 2-3 days.

Figure 1. Levels of dioxins and dl-PCBs in grass samples taken 1 day after the fire. Wind came from the east. The distance between the fire and point G is about 0.8 km.

Weurt
End of October 2010, a fire occurred at a meat packaging company in Weurt. Although initially unsuspected, chlorine levels on air filters were rather high and warranted the analysis of grass samples for dioxins and dl-PCBs. It turned out that a huge amount of plastic materials was present at the company for transport and packaging of the meat. The nearest agricultural area affected by the smoke was about 0.5 km away. Levels in samples taken during the final stage of the fire revealed dioxin levels up to 1.9 ng TEQ/kg (88% dm) in grass from a pasture at 0.6 km from the fire. This is 2.5 times the EU-limit for grass used as animal feed of 0.75 ng TEQ/kg. The level of dl-PCBs was 0.3 ng TEQ/kg. At a reference location south of the fire, the levels for dioxins and dl-PCBs were 0.4 and 0.3 ng TEQ/kg, suggesting that the dl-PCBs did not derive from the fire. Follow-up during several weeks did not show a significant decline in the levels despite the large amount of rain during this period. In a sample taken one month after the fire (end of November), the dioxin level at the location at 0.6 km even increased to 2.4 ng TEQ/kg. However, at this time also the reference location showed an

increased level of 0.9 ng TEQ/kg. This increased level is observed more often in winter time and can be explained by deposition during the winter and the lack of growth of the grass during this period. At this time point also a sample was collected from grass near a ditch at about 0.1 km from the fire. The dioxin level was 11.3 ng TEQ/kg, the dl-PCB level 0.8 ng TEQ/kg. It seems essential to collect samples close to the fire in order to strengthen a possible relationship with the fire.

Moerdijk

One of the largest incidents during the last decade occurred in the beginning of January 2010. A company with large volumes of all kinds of chemicals burnt down completely with a large number of explosions. The fire was covered broadly by Dutch television and caused a major concern for possible consequences for inhabitants and farms downwind of the fire. Fortunately, the nearest farms were 2.5 km or further away due to the Hollands Diep, a broad river directly north of the fire. A large number of grass samples were collected in the potentially affected area shortly after the fire. A sample opposite of the fire at 2.5 km showed dioxin and dl-PCB levels of 7.1 and 0.9 ng TEQ/kg. Many other samples collected in an area up to 10 km from the fire showed dioxin levels between 1.1 and 2.4 ng TEQ/kg and dl-PCB levels of 0.2 to 0.4 ng TEQ/kg. Samples were also collected at two other locations at the unaffected side of the fire. A first sample, taken on the industrial site, showed dioxin and dl-PCB levels of 4.6 and 9.5 ng TEQ/kg. Two other samples, taken West of the fire in a more agricultural area but close to a road showed dioxin levels of 3.5 and 4.3 ng TEQ/kg, and dl-PCB levels of 0.9 and 0.9 ng TEQ/kg. Five farms in this area were resampled, taking samples in pastures. The average dioxin level was 1.9 ng TEQ/kg (range 1.5-2.5). The levels of dl-PCBs was 0.4 ng TEQ/kg (range 0.4-0.6). This demonstrates that it is tricky to conclude whether increased levels are really due to a fire, especially in winter time. A large number of Brussels sprouts and curly kale were also analysed but none of these showed an elevated dioxin or dl-PCB level.
The incident opened up the discussion on the potential consequences of feeding grass with levels 2-3 times the limits to cows and especially sheep. A major question is whether carry-over factors for dioxins from fires are similar to those from other incidents with feed. This will be part of future studies.

Lith

In September 2011, a storage facility of a company supplying silos and plastics for farms burned down completely. The materials included a large amount of PVC. Being a known source of dioxins, samples of grass and corn from fields adjacent to the fire were sampled one day after the fire. A grass sample from a lawn next to the fire showed a dioxin level of 43.6 and dl-PCB level of 5.5 ng TEQ/kg. A corn sample taken at 0.1 km from the fire showed dioxin and dl-PCB levels of 1.8 and 0.4 ng TEQ/kg. The grass was not intended to be used as feed but the corn was turned into silage for feeding of dairy cows. Regarding the relatively high level, exceeding the feed limit, it was recommended not to use the material as feed. Part of the material was used to perform a carry-over study with dairy cows.

Congener patterns

Figure 2 shows the congener patterns of the samples with the highest observed dioxin levels in each of the four cases, expressed as relative contribution to the TEQ-level. It is clear that patterns are remarkably similar, with the exception of Moerdijk. In the other 3 cases PCDFs and in particular 2,3,4,7,8-PeCDF contribute most to the TEQ-level. When applying the new TEFs of 2005, the contribution of 2,3,4,7,8-PeCDF will slightly decrease to around 30%. The quite different pattern in the case of Moerdijk, which also differed from other samples taken during this incident, implies that the fire may not be the cause of the elevated level in this sample. The actual location was a small shipyard and other sources seem possible.
The relative high contribution of 2,3,4,7,8-PeCDF and other lower chlorinated PCDD/Fs is of importance since these show relatively high absorption and carry-over rates to milk and eggs. This was confirmed by preliminary results from a carry-over study with contaminated corn silage from the fire in Lith. Levels in the corn were around 1 ng TEQ/kg (88% dm) and within 5 weeks resulted in milk levels around the limit.

Conclusions

The present data show that levels in grass taken close to a fire (<0.2 km) can contain very high levels of dioxins which would certainly cause increased levels in e.g. milk, eggs and meat when fed to animals. At somewhat higher distances, up to 1-2 km, levels may still be elevated compared to the normal background levels and even

exceed the EU-limits for feed. Prolonged feeding of such materials like grass and corn could certainly result in an increase in the levels in e.g. milk and eggs. If the materials are not harvested and are still growing, there will be a gradual dilution of the levels and this will counteract the gradual increase in the levels in milk and eggs observed when feeding material with a constant level of dioxins. Precipitation does not seem to affect the levels in grass which may be explained by the lipophilic nature of these compounds.
A particular issue is the situation in late autumn and winter. At this time of the year, dairy cows are normally kept inside and grass in pastures is not a feed commodity for these animals. The situation is different for certain types of meat cows and especially for sheep which in principle are kept outside during the whole year. The elevated levels in the winter grass may be one of the reasons that sheep meat and especially livers often show relatively high levels of dioxins. The carry-over of dioxins and PCBs in both lactating sheep and meat sheep is currently under investigation, partly within the EU-project QSAFFE.
It can be concluded that fires may cause an increase in dioxin levels in grass and other feed commodities in the direct surroundings and that measures to prevent increased levels in animal derived food products are warranted. Rapid analyses of samples by GC/HRMS, possibly supported by screening assays, is required to reduce the potential effects on both consumer and animal health and economics of affected farms.

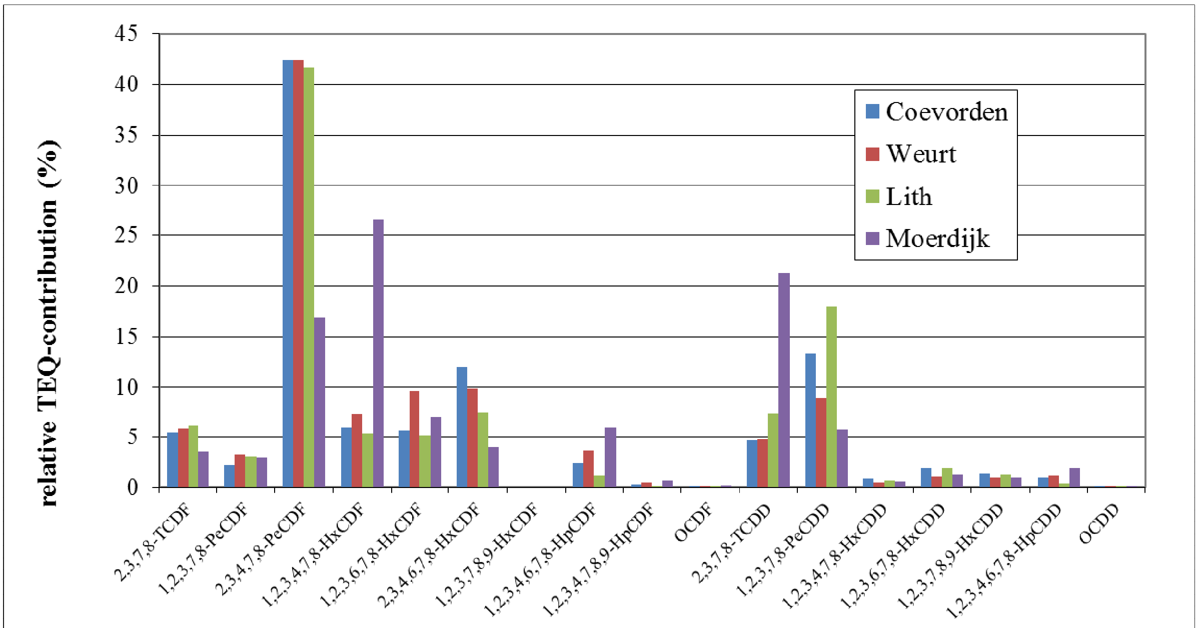

Figure 2. Congener patterns of dioxins in grass samples with the highest observed levels during the incidents in Coevorden (219 ng TEQ/kg), Weurt (11.3 ng TEQ/kg), Lith (43.6 ng TEQ/kg) and Moerdijk (7.1 ng TEQ/kg). Levels are expressed as relative contribution to the TEQ-level using TEFs 1998.

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References

1. Marklund S, Anderson R, Tysklind M, Rappe C (1989) *Chemosphere*. 18; 1031-8.
2. Draper W, Phillips J, Harnly M, Stephens (1988) *Chemosphere* 17; 1831-50.
3. Hoogenboom L, Van Eijkeren J, Zeilmaker M, Mengelers M, Herbes R, Immerzeel J, Traag W (2007) *Chemosphere* 68; 814-23.
4. EC (2006) *Off. J. Eur. Union*. L32, 44-53.
5. Hoogenboom L, Bovee T, Portier L, Bor G, van der Weg G, Onstenk C, Traag W (2004) *Talanta* 63; 1249-53.