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BIOMONITORING AND SOURCE TRACKING OF DIOXINS IN THE NETHERLANDS

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Introduction

In the region of Harlingen, situated in the north of the Netherlands, people are becoming very concerned about adverse health effects related to the possible emission of dioxins and other POPs by a waste incinerator installed in 2011. Biomonitoring programs in eggs and grass show serious local pollution with dioxins and dl-PCBs in the environment. Within a time span of only one year analysis of long-term sampling of flue gas of the incinerator show a strong relation to the congeners found in the eggs of backyard chicken and grass. But most important long-term sampling shows exceeding emissions values during unstable combustion situations in start-ups, shutdowns and failures not detected in regulatory short-term sampling.

Materials and methods

Harlingen is a small city (approx. 16,000 inhabitants), situated near Wadden Sea (Unesco World ecological marine heritage site), in an agricultural area with some small industries (relatively low-profile, mainly concentrated near the harbour). These industries consist an oil company, shipyards, fishing industry, a plastic company and a waste incinerator built in 2011. The eggs of backyard chickens were sampled at 15 different locations near Harlingen and analysed. The eggs were analysed for dioxins (PCDD/Fs) and dioxin-like polychlorinated biphenyls (dl-PCBs) by DR CALUX# (Dioxine Responsive Chemical Activated LUCiferase gene eXpression), BioDetection Systems [1], Amsterdam and RIKILT, Wageningen, the Netherlands. GC/HRMS analysis: Eggs: MAS (Münster, Germany), RIKILT Wageningen and Nofalab Schiedam (both in the Netherlands). Flue gas: AMESA continuous sampling by the Environment SA [2], analyses of the samples by Eurofin, Germany. The obliged analyses of the REC flue gas were done by SGS (Belgium). Grass samples by the RIVM (National Institute for Public Health and Environment in the Netherlands), analyses RIKILT, Wageningen. All labs are ISO17025 accredited according to the EC/252 guideline.

Results and discussion

The results of the DR CALUX# bioassay at 15 locations for backyard chicken eggs, nearby Harlingen harbour showed a serious pollution of dioxins in the environment of the incinerator (Figure 1). Levels of dioxins and dioxin-like PCBs are increasing toward the harbour. A subsequent comparative study in the Netherlands [3] shows 48% of the eggs of backyard chicken can be compliant the limit value of dioxins. In the region of Harlingen, none of the backyard eggs could be found to be compliant (n=6 verification with GC/MS).

Several factors contribute in local plume stacks, indicating insufficient spreading in air and environment: a short chimney (44 metres), windmills in the proximity and coastline fumigation. In the next study the short-track deposition of dioxins around the incinerator on grass was measured. Reference locations were taken a few kilometres from the incinerator. In figure 2 the results show the highest levels near the incinerator, indicating the incinerator as source of the PCDD/Fs.

To investigate the dioxin emissions of the incinerator a long-term sampling program (AMESA) was used to measure the flue gas in the chimney of the incinerator. Regulatory only 12 hours, representing only 0,1% of the yearly operating time, is obliged to determine the yearly dioxin emissions. In figure 3 the results of the short-term sampling (8 measurements in 4 years) show no consistent pattern and only in 50% of the cases only some congeners could be measured. Measurements are done under normal operating conditions and not during unstable combustion. Results of long-term sampling (Figure 4) are much more consistent than the short-term sampling.

A huge benefit of working with continuous measurements is detecting dioxins emissions during processes of start-ups, shutdowns or failures in the APCD (Air Pollution Control Devices) or combustion temperatures. In October 2015 the total TEQ of the flue gas exceed with 0.17 ng TEQ/Nm³ the European standard of 0.1 ng TEQ/Nm³ and a factor 17 with the Dutch Guidelines Industrial Emissions (RIE) of 0,01 ng TEQ/Nm³. The high dioxin emissions could be related to a standard start-up procedure with

structural bypassing of the fabric filter. Due to continuous measurements revealed dioxins emissions in flue gas otherwise never would have been detected. This makes it highly recommended to perform continuous measurements in all incinerators (of the Netherlands). Short-term measurements cannot be capable for estimating the real emissions of dioxins. In case of the incinerator of Harlingen, 35 times start-ups since the start of installation in 2011 have been occurred. A point of attention is the relative high percentage (33%) of dl-PCBs in the total concentration of PCDD/F/dl-PCBs in flue gas. Normally the dl-PCBs fraction contributes only a few percent in the TEQ of the flue gas. The REC incinerator PCB 126 counts 10% of the total TEQ. The flue gas also contains brominated flame retardants (BFRs), polybrominated diphenyl ethers (PBDEs) and perfluoro-octanoic acid (PFOA). Under unstable conditions also brominated dioxins (PBDD/Fs) were found. In the ninth month of the one year program of continuous measurements (2016) again an exceeding of the limit value was observed, without a start-up, shutdown or failure. This contributes to the hypotheses the combustion temperatures not met the regulatory values on the 2 seconds combustion level (above 8500/11000). So far the temperature data are not given by the management of the incinerator, so there's no complying with the rules set up by the Stockholm Convention (2004).

Figure 5 shows the congener patterns of eggs, grass and flue gases. The tetra-congeners show a lesser contribution, but can be possible explained by metabolism or biotransformation processes. For the other congeners, there is a qualitative match with those found in the incinerator.

Conclusions

The results of this research show the eggs of backyard chickens as a highly sensitive biomarker for dioxins/PCBs. This is also confirmed in other publications of contamination in the vicinity of potential sources (harbour activity, waste incinerator, landfill) [4]. In the special case of this incinerator REC in Harlingen grass could be used as biomarker, but only due to the short distance characteristics of this installation (short chimney, windmills and shoreline fumigation). The congener patterns of flue gas match the patterns found in eggs and grass.

Long-term sampling showed far more accurate flue gas emissions than the short-term measurement of flue gas. It is obvious that elevated dioxin emissions cannot be measured by the short-term sampling of dioxins. Under normal conditions, the incinerator complies with emission standards, but inadequate start-up procedures, shutdowns and failures in APCDs make incinerators a substantial source of PCDD/F/dl-PCBs, brominated and fluorinated compounds. Not releasing the temperature data seems contrary to the international agreements of the Aarhus (1998) and the Stockholm Convention (2004). This study is an appeal towards the scientific world to work together and find solutions for a still ongoing pollution.

Acknowledgements

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References

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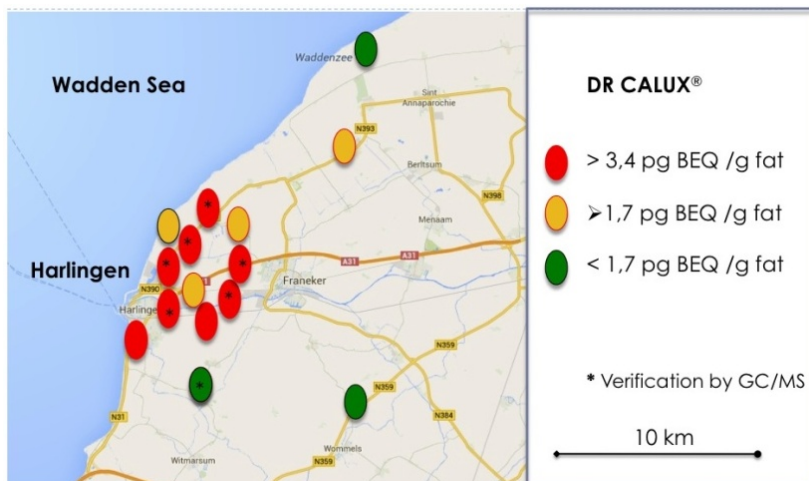


Figure 1: Dioxins in eggs of backyard chickens near Harlingen

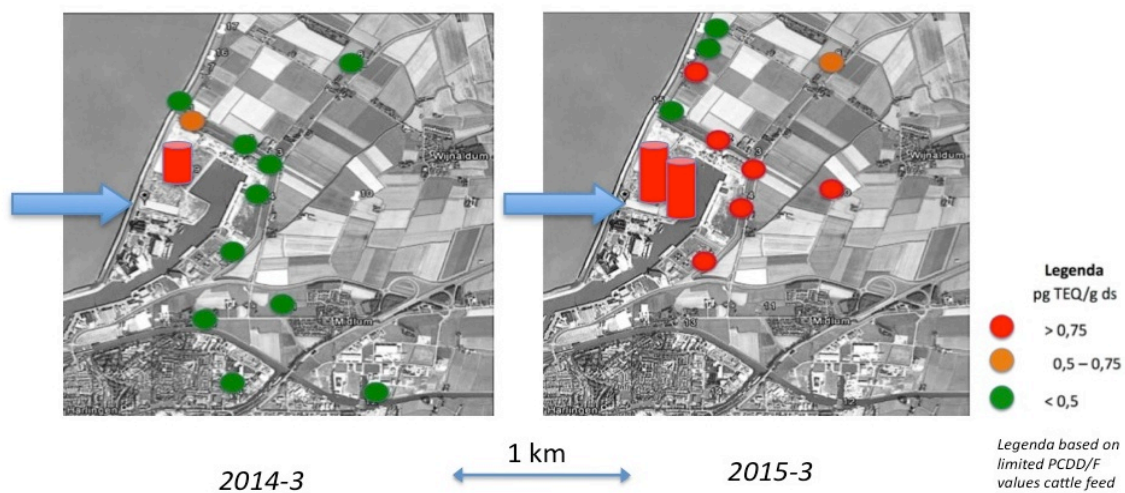


Figure 2: Dioxins in grass around the incinerator REC, 2014 and 2015

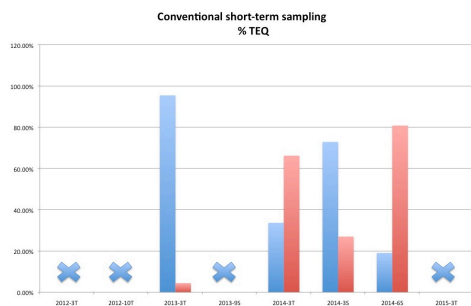


Figure 3: Short-term sampling of the incinerator

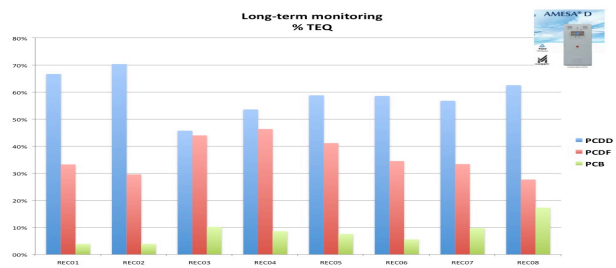


Figure 4: Long-term sampling

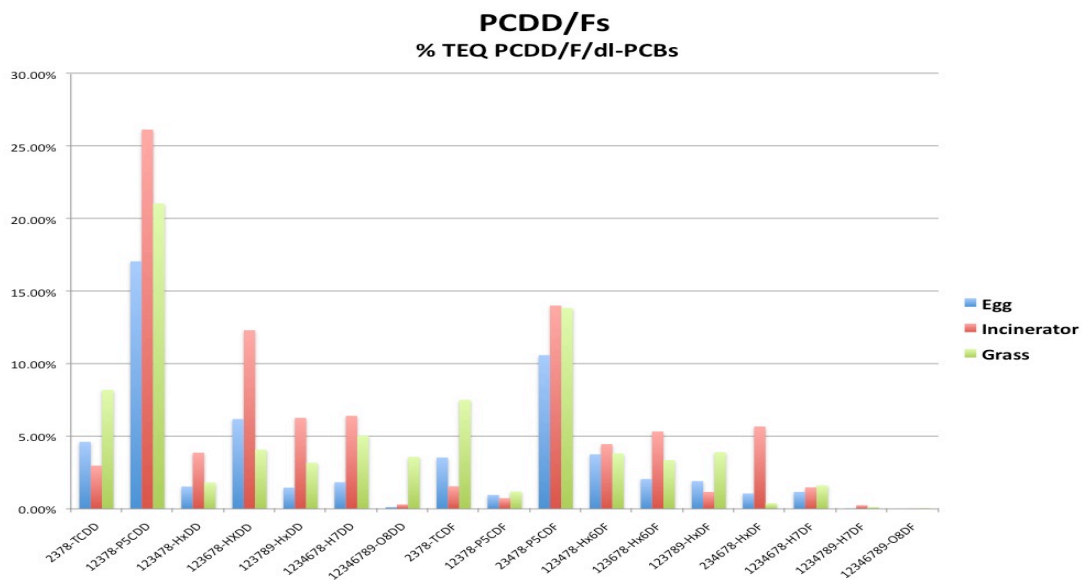


Figure 5: Congener patterns eggs backyard chicken, grass and flue gas incinerator REC