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Dioxin levels in fertilizers from Belgium: Determination and evaluation of the potential impact on soil contamination

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HIGHLIGHTS

- Several fertilizers available in Belgium were sampled and analyzed for their dioxin content.
- The measured dioxin contents were lower than what was already described in the literature.
- Estimations were made on the impact of fertilizer use on the possible dioxin contamination of agricultural soils.
- Common fertilization practices are safe.

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ABSTRACT

Dioxins are harmful persistent organic pollutants (POPs) to which humans are exposed mostly via the consumption of animal products. They can enter the food chain at any stage, including crop fertilization. Fertilizers belong to several categories: synthetic chemicals providing the essential elements (mostly N, P and K) that are required by the crops but also organic fertilizers or amendments, liming materials, etc. Ninety-seven samples of fertilizers were taken in Belgium during the year 2011 and analyzed after a soft extraction procedure for polychlorinated dibenzo-*p*-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) and dioxin-like polychlorinated biphenyls (DL-PCBs) using GC-IDHRMS. Only small qualitative differences could be observed between the main fertilizer categories since the PCDD:PCDF:DL-PCB average ratio obtained with the results expressed in TEQ was often close to 30:30:40 (typically for sewage sludge) or 40:30:30 (typically for compost). The median dioxin levels determined were generally lower than recorded previously and were the highest for sewage sludge and compost (5.6 and 5.5 ng TEQ/kg dry weight (dw), respectively). The levels in other fertilizers were lower including manure for which the median value was only 0.2 ng TEQ/kg dw. Several fertilization scenarios relying on the use of those fertilizers were assessed taking into consideration the application conditions prevailing in Belgium. From this assessment it could be concluded that the contribution of fertilizers to the overall soil contamination will be low by comparison of other sources of contamination such as atmospheric depositions. At the field scale, intensive use of compost and sewage sludge will increase dramatically the dioxin inputs compared with other fertilization practices but this kind of emission to the soil will still be relatively low compared to the dioxin atmospheric depositions.

1. Introduction

Large amounts of fertilizers are used in agriculture in order to increase the nutrient content of soil as required for optimal crop production. The most common fertilizers used are mineral chemicals that provide nitrogen, phosphorus and potassium to the plant (the so-called NPK fertilizers). In Belgium, quantities of mineral fertilizers used in agriculture range from 0 to 350 kg N, 0 to 150 kg P_2O_5 and 0 to 300 kg K_2O/ha/year. For the year 2008, it was estimated that 149,000 t N, 23,000 t P_2O_5 and 55,000 t K_2O were used in Belgium, which is somewhat lower than the years before (IFA, 2011). Besides the mineral fertilizers there is also an important use of farm manure as

Abbreviations: DL-PCB, Dioxin-like polychlorinated biphenyl; PCDD, Polychlorinated dibenzo-*p*-dioxin; PCDF, Polychlorinated dibenzofuran; POP, Persistent organic pollutant; TEQ, Toxic equivalent quantity.

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well as other organic fertilizers such as compost or sewage sludge (i.e., the bio-solid obtained by the processing of water in municipal or industrial wastewater treatment plants). An estimated of 228,000 t of nitrogen are produced each year in Belgium through animal excrements (Dumortier et al., 2012). This roughly corresponds to 834,000 t of pig manure, 254,000 t of poultry excrements and 4,458,000 t of bovine manure. Compost and manure application rates are limited by the nitrogen content of the product. They are generally spread on soil at rates of several tons/ha, using a solid manure spreader. In Belgium, about 500,000 t of compost are produced each year. Among them, about 100,000 t are used in agriculture and 11,000 t are used in horticulture (VLACO, 2009; SPW DGO-3, personal communication).

Two main sludge categories are used as fertilizers; (i) sewage sludge coming from urban wastewater treatment plants, and (ii) sludge coming from the treatment of agro-industrial wastewater. These sludge categories have different contaminant contents, and hence must be studied independently. Two kinds of industrial sludge are regarded with special care; (i) paper mill sludges because they are the most abundant, and (ii) decarbonatation sludges produced by the cleaning of surface water because they differ strongly from the other types of industrial sludge. While there are different regulations for the Flemish, Walloon and Brussels regions, applied quantities are generally under 4 t of sludge per ha and per year on crops and below 2 t of sludge per ha and per year on meadows. Moreover, the use of urban sludge in agriculture is strictly forbidden in the Flemish Region. According to the Federal Public Service Health, Food chain safety and Environment about 116,000 t of sludge (dry weight) were spread on Belgian agricultural soils in 2008.

Nowadays, there is a lot of controversy about the use of organic fertilizers such as sludge owing to possible contamination by various pollutants such as trace metals, polycyclic aromatic hydrocarbons, polychlorinated biphenyls, dioxins and other contaminants (Engwall and Hjelm, 2000; Renner, 2004; Pritchard et al., 2010; Nabulo et al., 2011). In the present paper our interest was focused on the presence of dioxins in fertilizers, and its potential impact on the food chain. Polychlorinated dibenzo-*p*-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) and coplanar polychlorinated biphenyls (DL-PCBs) do exhibit “dioxin-like toxicity”, commonly expressed in toxicological equivalents (TEQ) (Van den Berg et al., 2006). Dioxins are classified as persistent organic pollutants (POPs) that can bioaccumulate in the food chain. Human exposure to dioxins is a matter of concern (Travis and Hattemer-Frey, 1987, 1991; Charnley and Doull, 2005) since these contaminants are responsible for several health effects involving impairment of the immune system, the nervous system, the endocrine system, and the reproductive functions and are suspected to promote cancer (Hester et al., 1996; European Commission, 2010).

Currently, there is no legal limit set for dioxin concentration in fertilizers at the European level. National legislations, however, do often impose PCB limits and even PCDD/F limits for bio-wastes. In Belgium, maximum levels of 0.8 mg PCBs/kg dry weight (dw) and 0.5 mg PCBs/kg dw are set for non-dioxin-like PCBs in organic fertilizers in the Flemish region (OVAM, 2005) and in the Walloon Region, respectively.

The main goal of the present work was to gather data on the actual dioxin concentrations in the various fertilizer categories available in Belgium in order to refine the risk assessment performed previously with data from the literature. We focused on the materials that are suspected to contain the highest concentrations in dioxins such as sludge and compost. Therefore, a total of 97 samples were taken all over the country and analyzed for their content in PCDDs, PCDFs and DL-PCBs.

2. Materials and methods

2.1. Sampling

In 2011, a total of 97 fertilizer samples were taken all over the country. The main fertilizer categories selected were the organic fertilizers. Sludge samples were taken from municipal wastewater treatment plants either in urban and rural areas (10 and 6 samples, respectively), from agro-industrial wastewater treatment plants (17 samples), from drinking water treatment plants (7 samples of decarbonation sludge), and from paper mills wastewater treatment plants (3 samples). The compost samples were taken from composting plants using fresh plant material (9 samples) or making compost from waste (7 samples). The digestate samples (9) came from anaerobic digestion of waste or energy crops. The manure samples were from bovines (6 fresh and 3 composted solid samples), pigs (3 slurries) and poultry (2 samples). In addition, a category of liming materials was considered, either by-product from sugar factories (4 samples) or other commercial products (4 samples). Finally, 7 samples from very different origins (ash, ground egg shells, blood and hair meal…) were put in the category “miscellaneous fertilizers”. In this category, there is also one sample containing a synthetic chemical fertilizer which was obtained by pooling 8 commercial fertilizers mixed in equal proportions (ammonium nitrate, ammonium sulfate (two different brands), potassium chloride, magnesium ammonium nitrate, bulk NP fertilizer, ammonium sulfonitrate and magnesium oxide). For the sake of clarity in the following sections, samples were splitted into 7 categories: sewage sludge; industrial sludge; compost; manure; digestate; liming materials and others.

The obtained samples were generally placed in 1 L glass jars. However, solid samples which could not be placed in a jar because of the significant presence of large solid fragments (solid manure or compost) were placed in polyethylene plastic bags. Moreover, some commercial fertilizers were stored in their original package. All samples were kept in the refrigerator before processing. Typical sampling scenarios were the following:

- Trailer loaded (e.g. sludge): Several sub-samples were gathered from the trailer surface (depth from 5 to 30 cm). At least 4 sub-samples were gathered per trailer according to their heterogeneity.
- Heap (e.g. liming materials, compost or manure): Several sub-samples were gathered from the heap surface (depth from 5 to 50 cm), ideally on the whole perimeter and at different heights. The number of sub-samples was chosen according to the heap size, going from 5 for small heaps (few cubic meters) to 20 sub-samples for big heaps (tens of cubic meters).
- Liquid products stored in pits (e.g. liquid manure): after mixing with a stick, at least 3 sub-samples were gathered, at low depth, using a bucket or jars.
- Liquid products stored in a tank (e.g. sludge and digestate): the product was generally available using a tap. When possible the product was automatically mixed in the tank.

2.2. Extraction and sample preparation

Sample extraction was carried out using a modification of the standard EPA Method 8290 for soil, sediment, and ash as described in Method 4435 since the extract had to be analyzed by both chemo-and bio-analytical methods. Briefly, the samples were freeze-dried in a lyophilsator LyoVac GT2, grinded and stored in brown amber borosilicate containers. The extraction was performed at room temperature by vortexing and sonicating the sample (2 g) in a 20/80 methanol/toluene (v/v) mixture with a matrix to solvent ratio of 1:5 (w/v) as described in Baston and Denison (2011). The extract was then filtered on a celite column (25 mL column, glass wool, celite and sodium sulfate on top), collected in a 50 mL centrifuge tube and the extraction process repeated 2 more times with 10 mL of pure toluene, along with a final 10 mL column rinse of toluene straight onto the 25 mL column to ensure adequate recoveries. The clean-up consisted of an acid destruction of acid degradable compounds followed by the removal of sulfur according to the standard EPA method 3660B. The digestion is performed by adding 2.5 mL of concentrated sulfuric acid to 5 mL of extract suspended in n-hexane. The extract is then transferred to an acid silica column (10 mL; 33% w/w acid/silica) containing activated copper with hydrochloric acid. The