Dioxin Compounds Emissions to Agricultural Soils Through the Use of Fertilizers, Soil conditioners and Sewage Sludge

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Introduction

PolyChlorinated Dibenzo-p-Dioxins (PCDDs), PolyChlorinated Dibenzofurans (PCDFs) and Dioxin Like PolyChlorinated Biphenyls (DL-PCBs) are known to exhibit "dioxin like toxicity" and are considered as potential threats for human health. Humans are mainly exposed to dioxin-like compounds through their environment or, to be more specific, through food consumption which is believed to be responsible for more than 95% of our total exposure[1]. Therefore, diet exposure to dioxins is a matter of increasing concerns and is subject to strict monitoring.

However, we have limited means to interfere with the dioxins levels in foodstuff, except from avoiding accidental contaminations. The historic contamination of our soils can only slowly decrease with time and many efforts have already been undertaken to decrease the atmospheric deposition. Up to now, very limited attention is given to the dioxins imissions to the food chain through agronomic inputs like fertilizers and soil conditioners.

Presently, there are no legal limits for dioxins and dioxin like compounds concentrations in fertilizers, soil conditioners and sludge in the European legislation. However, in the 3rd draft of the working document on sludge from the European Commission a limit of 100 ng TE/kg dw for PCDDs and PCDFs and a norm of 0,8 ng/kg dw for the sum of 7 reference PCBs (28, 52, 101, 118, 138, 153, 180) has been proposed[2]. National legislations are more restrictive, often imposing PCBs limits and sometimes even PCDDs and PCDFs limits for biowastes. This paper describes a methodology for the evaluation of dioxin like compounds imissions to agricultural soils.

Materials and methods

In order to assess dioxins imissions to the food chain associated with the use of fertilizers, sludge and soil conditioners, three models have been settled:

- ✓ Assessment of the quantities of dioxins spread on Belgian agricultural soils at country scale = Σ (Total product consumption throughout the country * Product dioxins' concentration) [g TEQ/year].
- ✓ Assessment of the maximal quantities of dioxins spread on agricultural soils at field scale = Σ (Maximal product consumption per ha * Product dioxins' concentration) [ng TEQ/ha.year].
- ✓ Assessment of the maximal quantities of dioxins directly sprayed on plants at plant scale = Σ (Maximal product consumption per ha * Product dioxins' concentration / Plant biomass dry weight (= 5T/ha in our scenario)). [ng TEQ/kg plant dw] (Liquid products which are sprayed on plants are directly contaminating crops).

Models input have been obtained from various sources. Applied quantities at each scale were evaluated according to available information from the literature, official and private statistics, communications with experts and federations or legislative limits. Information on dioxins' concentration was obtained from the scientific literature, avoiding out of date publications and studies with only few samples analyzed. For practical reasons, all TEQ systems (I-TEQ, WHO-TEQ and N-TEQ) are considered as equivalent and are thus simply referred to as TEQ, without any distinction.

Results:

The average dioxin-like compounds contamination for some major agronomic inputs which are used in our models is specified in table 1 with average soil contamination for comparison. This table highlights some gaps in the literature. Note that the mean, and not the median, was considered as the relevant parameter in our case.

Table 1. Products dioxins and dioxin-like compounds levels selected for this study.[3]

Products	Mean PCDD/PCDF concentration ng TEQ/kg dw	Mean DL-PCB concentration ng TEQ/kg dw	Dioxin and dioxin-like compounds ng TEQ/kg dw
NPK fertilizers	2,7 (**2**, 17)*	1.35 $^{\Delta}$	4.05
Micronutrients	80.6 (**1**, 17)	40.3 $^{\Delta}$	120.9
Compost & Digestate	18.9 (**9**, 551)	3.0 (**4**, 60)	21.9
Manure	1.58 (**2**, 16)	0.79 $^{\Delta}$	2.37
Liming materials	0.42 (**1**, 1)	0.21 $^{\Delta}$	0.63
Sludge	29.9 (**12**, 425)	14.6 (**5**, 134)	44.5
Belgian Agricultural Soils	2.35 (**2**, 5)	1.17 $^{\Delta}$	3.52

***Figures between brackets refer respectively to **the number of studies** and the number of samples involved.
$^{\Delta}$ No data available, default PCB levels were set at 1/3 of the total dioxin level.

The results from our first model are plotted in Figure 1. Total PCDDs/PCDFs and PCBs input to Belgian agricultural soils through fertilizing materials is estimated to reach 19.26 g TEQ/year, from which more than 3/4 is linked to manure and sludge application. To allow comparisons, total dioxins atmospheric depositions on agricultural soils are under 33.6 g TEQ/year (for PCDDs/PCDFs and PCB 126), considering 15 351 km² of agricultural soils in Belgium[4] and depositions below 6 pg WHO-TEQ/m².day[5].

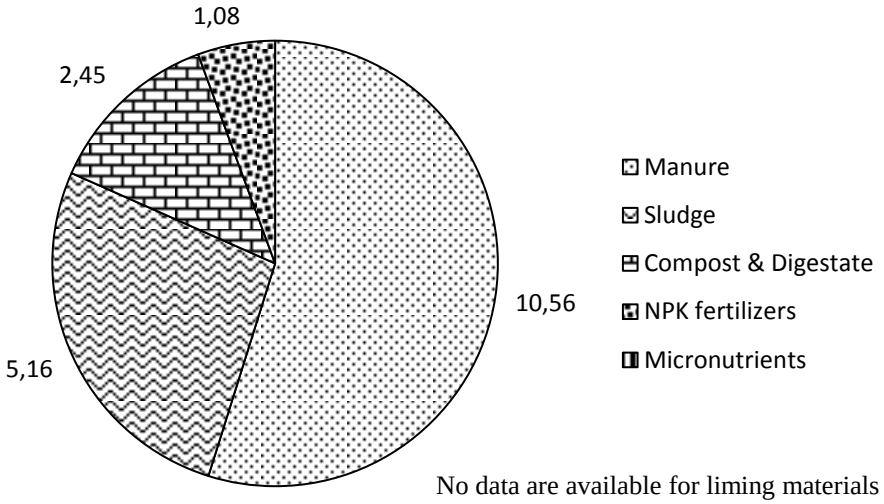

Figure 1. Dioxins input to Belgian agricultural soils (g TEQ /year).

Our second model gives some information at the field scale, considering maximal possible use for each product (worst case scenario). Results are shown in figure 2. Altogether, maximum fertilization rates could bring up to 393 000 ng TEQ/ha.year. Nevertheless, dioxins and dioxin-like compounds input through fertilizing materials could not significantly impact soil dioxins' content. Maximum fertilization rates could only increase by 2.3 % the soil dioxins' content for the upper 30 cm (considering 4800 tons of soil containing 3.52 ng TEQ/kg). It is important to notice that the worst case does strongly differ from the average case. In the average case, depositions are of 12544 ng TEQ/ha.year (= 19.26 g TEQ/15351 km²*10^7) which represents only 3.19% of the

maximum conceivable input and a 0.07% increase of the total soil dioxins' concentration. The difference between the worst and the average case can be explained by the seldom use of the more contaminated fertilizers.

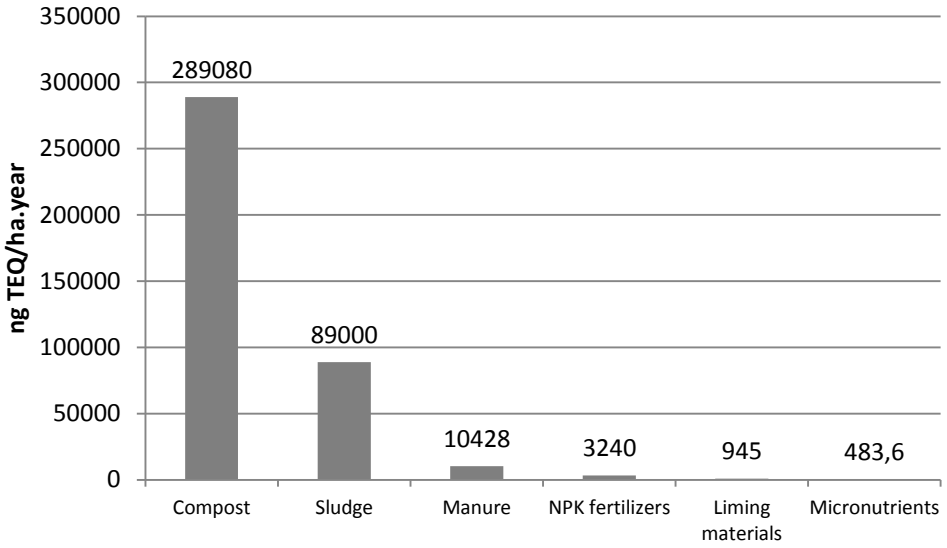

Figure 2. Maximum annual dioxins input at field scale.

Our third model pays more attention to some liquid products which could contaminate the food chain through direct plant contamination when fertilizers are directly sprayed on crops. The results are shown in figure 3. Our model overestimates the real contamination due to liquid fertilizing materials because a vast majority of the product runs off to the soil. Results from figure 3 can be compared to the European limit for PCDDs/PCDFs in feedstuffs: 0.75 ng WHO, 1997-TEQ/kg forage with 12 % moisture content (2006/13/EC). Atmospheric depositions (4.38 ng WHO-TEQ/kg plant dw) are also shown in this chart in order to allow comparisons.

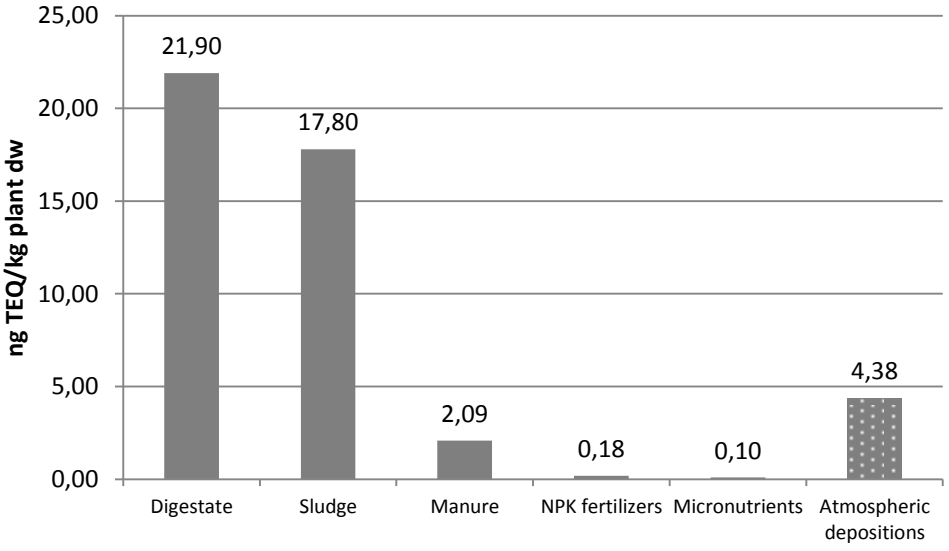

Figure 3. Maximum amounts of dioxins sprayed on plant leaves through fertilization and comparison with atmospheric depositions.

Discussion:

Fertilizers do not strongly increase soil dioxins' content. The maximum conceivable input from fertilizers, soil conditioners and sludge could only increase soil TEQ content by about 2.3% per year. However, dioxins are

Persistent Organic Pollutants (POP) and should therefore be considered with care. It is also important to add that besides atmospheric deposition, fertilizers, soil conditioners and sludge, dioxins can also be brought to agricultural soils by pesticides and accidental contaminations.

At the Belgian scale, manure and sludge are the major potential contributors to the soil dioxins' input while at the field scale compost and sludge could be major contributors. Moreover, digestate and liquid sludge could lead to higher risks when sprayed on plants rather than on soil. Globally, manure, sludge and compost & digestate are the major potential contributors to the global dioxin risk. Among these materials, distinctions should be made. Compost, digestate, manure and industrial sludge produced by food and feed industries are coming from agricultural soils and are simply going back to where they were removed from whereas sewage sludge for instance should be considered as an input from the outside.

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