

## Impact of heavy metals on human toxicity using LCA: The case study of Walloon corn<sup>★</sup>

Saïcha Gerbinet<sup>1,\*</sup>, Florence Van Stappen<sup>2</sup>, Sandra Belboom<sup>1</sup>, Eric Pezenec<sup>3</sup>, and Angélique Léonard<sup>1</sup>

<sup>1</sup> Chemical Engineering – Products, Environment and Processes (PEPS) – University of Liège, B6, allée de la chimie 3, 4000 Liège, Belgium

<sup>2</sup> Walloon Agricultural Research Centre, Chée de Charleroi 234, 5030 Gembloux, Belgium

<sup>3</sup> Knauf Insulation Sprl, Rue de Maestricht 95, 4600 Visé, Belgium

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**Abstract.** This paper focuses on potential errors when assessing the human toxicity of corn farming in Wallonia, Belgium. The USEtox method is applied to the farming of 1 hectare of corn. Local data are used for farming data and GaBi datasets for background data. Field emissions due to farming are calculated by the most prevailing models. The results in human toxicity, cancer effect, underline the large contribution of chromium (Cr) emissions. But when characterizing fertilizer composition, only the total chromium is measured and therefore unspecified chromium is used as emissions. However, it is known that chromium in the natural environment is mostly the non-toxic form Cr (III), which would greatly decrease the impact as the characterization factor for unspecified chromium is, in USEtox, the average of Cr (III) and the toxic form Cr (VI). The impact for human toxicity, non-cancer effect is mostly related to zinc emissions even if zinc is relatively harmless. The impact of pesticides is negligible in both cases. These results show that caution must be taken when examining/interpreting toxicity categories.

**Keywords:** Life Cycle Assessment / human toxicity / USEtox / corn / chromium / zinc

**Résumé. Impact des métaux lourds sur la toxicité humaine en analyse du cycle de vie : le cas du maïs en Wallonie.** L'objectif de cet article est de mettre en évidence les erreurs potentielles lorsque la toxicité humaine de la production de maïs wallon est étudiée. La méthode USEtox a été appliquée à la culture d'un hectare de maïs. Des données locales ont été utilisées concernant la culture alors que des jeux de données issus de GaBi ont été utilisés pour les données d'arrière-plan. Les émissions aux champs liées à la culture ont été calculées en utilisant les modèles recommandés actuellement. Les résultats dans la catégorie toxicité humaine, effet cancérigène, mettent en évidence la contribution très importante des émissions de chrome. Cependant, lorsque les compositions des engrais sont mesurées, seul le chrome total est dosé, sans spéciation. C'est pourquoi ses émissions sont renseignées comme émissions de chrome non spécifié. Néanmoins, dans l'environnement naturel, le chrome est principalement présent sous sa forme non-toxique, le chrome (III), ce qui pourrait fortement réduire l'impact puisque, dans USEtox, le facteur de caractérisation du chrome non-spécifié est égale à la moyenne du facteur de caractérisation du Cr (III), très peu toxique, et du Cr (VI), très toxique. Pour ce qui est de la catégorie toxicité humaine, effet non-cancérigène, l'impact est principalement lié aux émissions de zinc alors que le zinc est très peu dangereux pour la santé humaine. Dans les deux cas, la contribution des pesticides est négligeable. Ces résultats montrent qu'une prudence particulière est de mise lors de l'interprétation des résultats liés aux catégories toxicités.

**Mots clés :** analyse du cycle de vie / toxicité humaine / USEtox / maïs / chrome / zinc

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\* e-mail: [Saïcha.Gerbinet@uliege.be](mailto:Saïcha.Gerbinet@uliege.be)

## 1 Introduction

In this work, we want to emphasize the limitations that we observed when using databases or inventories and methodologies as black boxes. Sources of errors and misinterpretation are illustrated in the particular case of assessing the toxicity of heavy metals using the USEtox methodology [1,2] during the production of corn. Indeed, corn is an important cereal with many applications in the feed and food industries (e.g. starch production). To properly evaluate the environmental impact of its applications, for example in the growing context of bio-based products (such as in starch-based products), a better understanding of the impact of its production is needed, using Life Cycle Analysis (LCA). Any error made in the evaluation of the agricultural step could have a large impact on subsequent results obtained at the final product stage.

Contrary to REACH<sup>1</sup>, that is based on risk assessment, LCA evaluates potential environmental impacts associated with products. This leads to differences in estimation of toxicity. In the LCA field, studies have been performed and highlight the high uncertainties related to toxicity categories. For example, in their article, Pizzol et al. [3] examine the human health impact with nine different LCA methodologies, looking especially at the impact of metals. In their study, they consider 14 metals and compare their impact using different methodologies. The first conclusion is that the criteria used by LCA methodologies to include or not a specific metal in a toxicity category are unclear. Moreover, their analysis shows that the significance of each metal greatly varies with the chosen method. The USEtox model seems especially dissimilar in its results from any of the other models. With some case studies about waste management systems, the contribution of metals in human toxicity in USEtox is underlined. Other case studies have been published about the evaluation of toxicity, especially using USEtox [4,5]. For example, the study of Roos and Peters [5] focuses on textiles, but the contribution of metals is not investigated. The present study is the first one that focuses on human toxicity in the specific context of an agricultural product. In addition, there are many more studies assessing ecotoxicity but this is out of the scope of this work.

## 2 Materials and methods

### 2.1 The USEtox methodology

USEtox has been developed by the UNEP/SETAC Life Cycle Initiative for characterizing ecotoxicological and human impacts of chemicals. This is also the method recommended by the ILCD (International Reference Life Cycle Data System from the Joint Research Centre of the European Commission) to evaluate the toxicological

impact in an LCA [1–3,6]. Nevertheless, the method is classified as “Level III or interim” (recommended, but to be applied with caution) and this case study will show an example as to why. The method is available in most LCA software, for example in GaBi 7 [7] which was used in this work. The USEtox method also allows the user to define its own characterization factors for substances not yet included, and as illustrated by Roos and Peters [5] this could greatly affect the results. Nevertheless, in this study we only use the factors provided in the original method. The latest version of USEtox provides characterization factors labelled either interim or recommended. Interim characterization factors have higher uncertainties and should be used with caution. All the metals, for example, have interim characterization factors.

### 2.2 Case study: Corn production in Wallonia

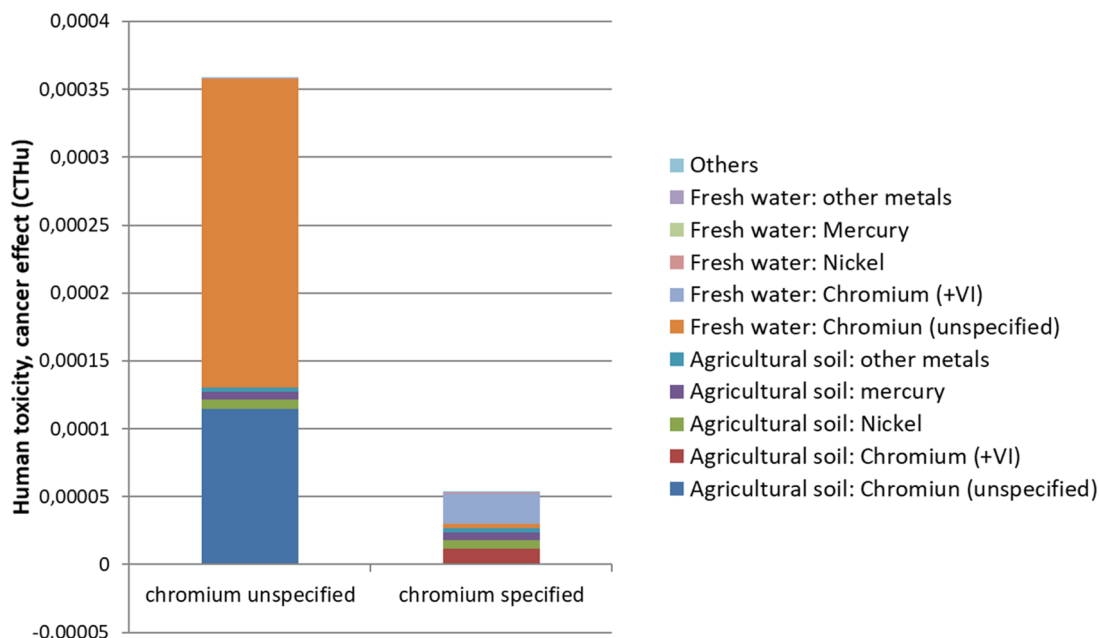
The studied system is the production of corn in Wallonia (South of Belgium). The primary data are taken from Van Stappen et al. [8]. The functional unit is 1 hectare of corn crop in Wallonia, and the LCI data are based on actual agricultural practices recorded in farms’ accounting data. The field emissions from the application of inputs were assessed by emission models as recommended by Nemecek [9], and the emission of trace metals were calculated using the SALCA-Schwermetall Swiss model developed by Freiermuth [10] and adapted to local conditions using the trace metal content of mineral and organic fertilizers provided by Piazzalunga et al. [11]. Pesticides were assumed to end up entirely in the agricultural soil. The system has been modelled in GaBi 7 [7] using GaBi datasets [12]. Belgian datasets have been preferred when available, and if not, European datasets have been used, and if no European dataset is available, then German ones have been used. More details about the system are available in Van Stappen et al. [8].

## 3 Results

### 3.1 Human toxicity, cancer effect: The case of chromium

The human toxicity, cancer effect impact of farming 1 hectare of corn in Wallonia is 3.59E-04 CTUh (comparative toxic unit for humans, the de facto unit for measuring human toxicity impacts), mostly due to chromium emissions in freshwater and in soil from the organic and mineral fertilizers, as illustrated in Figure 1. All chromium emissions are classified in chromium unspecified emissions due to the sole dosage of total chromium during the fertilizer analysis. However, chromium is present as Cr (+III) or Cr (+VI) and, depending on its oxidation level, its toxicological impact is completely different. Indeed, there is no impact for Cr (+III) but a tremendous one for Cr (+VI). In USEtox, the characterization factor for unspecified chromium is the average of the two, therefore is high [1]. Depending on the actual ratio of both forms of chromium, the impact could be wildly different. Cr (+VI) is a powerful oxidant and is therefore very reactive. In the presence of organic components, Cr (+VI)

<sup>1</sup> Registration, Evaluation, Authorization and Restriction of Chemicals (REACH). REACH is a regulation of the European Union that aims to improve human health and environment protection by reducing the risks of chemicals.



**Fig. 1.** Impact on human toxicity, cancer effects, of the farming of 1 hectare of corn in Wallonia: Influence of the speciation of chromium.

*Fig. 1. Impact sur la toxicité humain, effet cancérigène de la culture d'un hectare de maïs en Wallonie : influence de la spéciation du chrome.*

will quickly react and be reduced to Cr (+III). It is therefore realistic to assume that all the chromium from organic fertilizers is Cr (+III). Moreover, in mineral fertilizers, chromium mostly comes from the rocks used in their production, such as dolomite or phosphate rock. As chromium exists as Cr (+III) in the natural environment, the chromium in mineral fertilizers should also be Cr (+III) [11,13,14]. The speciation of chromium in fertilizers has been studied and always shows a very small portion of Cr (+VI), generally below 2% [15]. Finally, the report of Piazzalunga et al. [11] that provides the organic fertilizer composition clearly underlines that these compositions fulfill the European standards on fertilizer composition.

We tested the case where 95% of the chromium emissions from fertilizers is Cr (+III), and with this change, the impact in the aforementioned category is divided by 7. Even so, the Cr (+VI) emissions in agricultural soil and freshwater still have the largest impact contribution (62%), as illustrated in Figure 1. The other main contributors are other heavy metals emissions to agricultural soil, mainly nickel (12%) and mercury (10%).

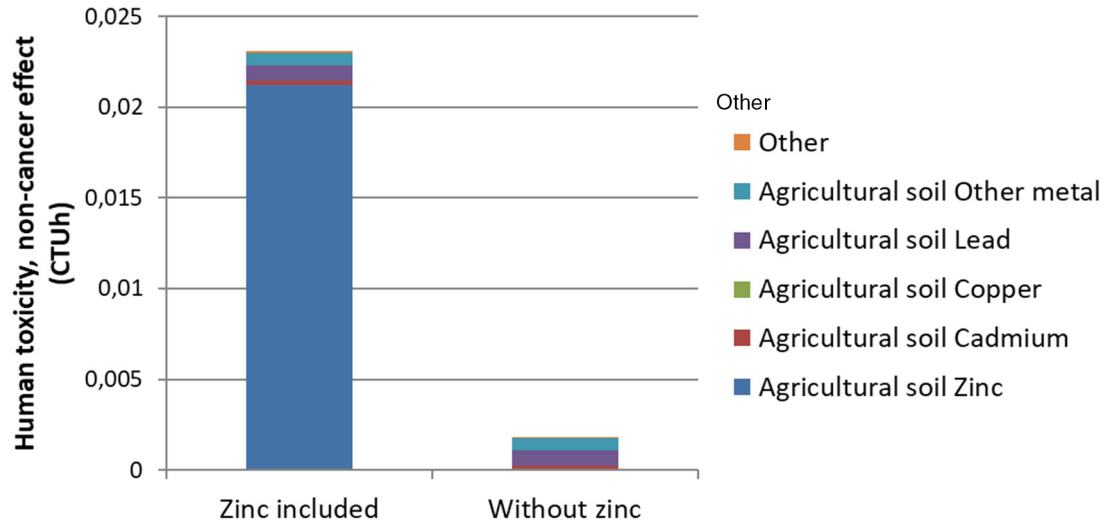
It is also interesting to note that the emissions of phytosanitary products in the soil contribute to less than 1% of the total impact on human toxicity. However, the total amount of phytosanitary products used, in mass, is larger than the amount of metal emissions in soil, water and air. This is because some of the phytosanitary products do not have characterization factors. Considering around 2.2 kg of pesticides (all included) are applied by hectare, only 1.2 kg is characterized in USEtox. The impact of the other pesticides is not taken into account. Moreover, most of them only have characterization factor in human toxicity non-cancer effect, such as glyphosate, even though

it is classified as probably carcinogenic for humans by the World Health Organization [16]. Finally, the characterization factors of the pesticides and other phytosanitary products are small compared to that of metals for emissions in agricultural soil. In this study; atrazine is the one with the larger characterization factor ( $1.3 \times 10^{-6}$  CTUh/kg), but is still smaller than all the metals included in this category.

### 3.2 Human toxicity, non-cancer effect: The case of zinc

The human toxicity, non-cancer effects of farming 1 hectare of corn in Wallonia is 0.0231 CTUh. It is mostly related to zinc emissions in soil, as underlined in Figure 2. In our case study, it is the metal with the largest emission in soil due to the organic fertilizers, and in a lesser extent to mineral fertilizers. The large amount of zinc in organic fertilizers mostly comes from the use of pig manure, which is rich in zinc because zinc supplements are given to pigs to accelerate their growth (it helps to stimulate the activity of certain enzymes), even though only 5% of this zinc is absorbed, on average, by the pigs.

Zinc is abundant and is an important trace element in the human body. It is useful for growth, bone and brain development, etc. and the European Commission recommends the consumption of 7–10 mg of zinc by person and per day. Moreover, mammals are able to eliminate excess zinc and maintain a constant level independently of the exposure. Consequently, the potential of zinc bio-accumulation is low for mammals, but this is not the case for the soil and vegetables, where the zinc can accumulate and interfere with the absorption of other metals [17–20].



**Fig. 2.** Impact on human toxicity, non-cancer effects of the farming of 1 hectare of corn in Wallonia: Influence of zinc.

**Fig. 2.** Impact sur la toxicité humaine, effet non-cancérogène de la culture d'un hectare de maïs en Wallonie : influence du zinc.

For humans, only the exposure to high doses can have toxic effects because it interferes with the uptake of copper [17–20]. On the other hand, some zinc compounds such as zinc chloride can be toxic. Therefore, this high contribution of zinc to non-cancerous toxicity for humans is quite surprising. In USEtox, the characterization factors are calculated by multiplying the effects expressed in cases/kg<sub>intake</sub> by the intake fraction expressed in kg<sub>intake</sub>/kg<sub>emitted</sub>. The intake fraction is the fraction of the emission that is taken by the overall exposed population. The effect factor of zinc is small in comparison to other metals; however, its characterization factor for emissions in agricultural soil is especially high because its intake fraction is high. The high contribution of zinc in human toxicity, is also underlined by the study of Querini et al. [4].

A test was made with the characterization factor of zinc equal to 0 in the USEtox model. In this case, human toxicity, non-cancer effect drops to 0.00179 CTUh (a 92% reduction), mostly from lead and mercury emissions in the soil.

The same observation can be made for the pesticides: their impact is smaller than 1%. Some tests were made with ReCiPe and the impact of pesticides is always small compared to that of heavy metals, whatever the cultural perspectives considered [1,2]. Other tests were performed using USEtox 2.01. Two situations have been investigated, in the first only the recommended characterization factors were considered, and in the second both recommended and interim characterization factors were used. All the factors for metals are classified as interim, as those for dissociating substances and amphiphilics. For the other substances, recommended characterization factors are based on chronic and subchronic effects, while those based on sub-acute data are classified as interim. If only the recommended characterization factors are considered, the score for corn production in human toxicity is strongly reduced and the impact fraction of pesticides becomes significant. In both cases, the impact from pesticides remains similar, but since most of the impact from other elements are interim, the

total impact in human toxicity, non-cancer effect is  $2.32 \times 10^{-7}$  CTUh when using only the recommended factors, and 98% of this impact is from the pesticides.

## 4 Discussion and conclusions

This work underlines the uncertainties related to the characterization of human toxicity in LCA. The impact of certain metals are as high as the inaccuracy of their measurements (unspecified chromium in human toxicity, for example), or can even seem incorrect (zinc in human toxicity, non-cancer effect). Moreover, the contribution of pesticides is negligible even if large amounts are used and emitted. In general, determining the toxicity of metals is difficult because their impact depends on their speciation, and their bioavailability within the environment makes the determination of a characterization factor difficult. Moreover, the high persistence of metals in the environment increases the uncertainties [3,4].

Although the uncertainties about toxicity categories are well-known, this case study underlines the impact of the user hypotheses and shows that a detailed analysis of the results is essential for a critical view on the toxicity results. Without a detailed analysis, results can be misinterpreted in all related problems: misplaced effort to reduce the impact, problem when comparing products, etc. The understanding of how the LCA method deals with toxicity categories and the issues of metals is of tremendous importance for a correct interpretation of the results, and sensitivity analyses on the methods should be conducted [3]. This article shows that the recommendation about a significant level of difference in toxicity categories should be increased from one order of magnitude, in the present recommendation of Jolliet [21] to several orders of magnitude. Another possibility could be to separately investigate the impact of organics and inorganics in toxicity categories as suggested by Querini et al. [4]. More investigation on that topic is clearly necessary.

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