Cadmium content of phosphate fertilizers used for tobacco production
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Abstract – Tobacco (*Nicotiana tabacum* L.) leaves may accumulate relatively high levels of cadmium (Cd). The presence of cadmium in soils originates from both natural and anthropogenic sources. In particular, phosphate fertilizers can contain high Cd levels due to the presence of cadmium in the phosphate rock used for their manufacture. In order to investigate the Cd concentration in phosphate fertilizers used for tobacco production, fertilizers were sampled worldwide and analyzed for Cd and phosphorus. Concentrations ranged from 0.08 ± 0.14 to 97.50 ± 8.74 g Cd/t P₂O₅. In some cases, these levels could be explained by the phosphate rock origins. Some of the Cd contained in the fertilizer appeared bioavailable, as determined by diethylenetriaminepentaacetate (DTPA) extraction. Although the bioavailability of the Cd added through these sources to the tobacco plants in the field is not known, the use of fertilizers containing high Cd concentrations should be avoided to protect the soil from gradually accumulating this element and to avoid possible additional Cd presence in crops. Therefore, while several strategies may be followed to reduce the Cd concentration in tobacco leaves, the implementation of new agricultural practices such as the screening of the fertilizer source may also contribute to reducing further soil accumulation of Cd.

cadmium / fertilizers / phosphate rock / heavy metals / *Nicotiana tabacum* / tobacco

1. INTRODUCTION

Cadmium (Cd) is a potentially very toxic metal (WHO, 1992) which is classified as a Class I human carcinogen by the International Agency for Research on Cancer (IARC, 1993). In humans, long-term exposure to Cd may lead to adverse health effects (Satarug and Moore, 2004; WHO, 1992). Environmental health concerns have been raised as various anthropogenic activities have led to the addition of significant quantities of Cd to agricultural soils (Wagner, 1993).

In particular, phosphate fertilizers represent a potentially significant source of Cd to the field. Indeed, they can contain high Cd levels due to the presence of the metal in the phosphate rock used for their manufacture (McLaughlin et al., 1996). Almost all phosphate fertilizers are produced from phosphate rock. The extent to which Cd originally present in the phosphate rock is transmitted to the final product may partly depend on the manufacturing process (Van Kauwenbergh, 2002). The Cd contents of phosphate rocks from various deposits have been published, and large differences may exist between deposits; especially, but not exclusively, between sedimentary and igneous phosphate rock (Van Kauwenbergh, 1997, 2002). Concentrations of Cd in several commercial fertilizers have also been monitored (e.g. de López Camelo et al., 1997; Franklin et al., 2005; Gabe and Rodella, 1999; Mishima et al., 2004). The use of high Cd-containing fertilizers may thus cause an accumulation of the metal in the soil, which may in turn be transferred to agricultural products. In this respect, risk assessments have been performed for the presence of Cd in P fertilizers (e.g. Hutton and de Meeûs, 2001; de Meeûs et al., 2002).

As for the majority of all crops, P fertilizers are commonly used for tobacco production (e.g. *Nicotiana tabacum* L.) production and the repeated use of Cd-containing P fertilizers may lead to progressive Cd accumulation in the tobacco field (Fig. 1). For instance, Semu and Singh (1996) reported a significant Cd enrichment of tobacco soils that received high P fertilizers for many years.
and Bielinska et al. (1999) reported that the application of 240 kg NPK fertilizer/ha in fields (i.e., 30 kg N, 90 kg P₂O₅ and 120 kg K₂O/ha, respectively) under tobacco cultivation led to an enrichment of Cd in the 5–20 cm topsoil when compared with the use of 700 kg Flovit fertilizer/ha (NPK formula of Flovit: 4-12-18). The Cd content of the fertilizers used in these studies was not given.

The goal of this survey was to investigate the Cd concentration in various commercial P fertilizers used for tobacco production and obtain information on the origin of the phosphate rock used to manufacture these fertilizers. This may assist us in identifying fertilizers that may pose a potential problem for Cd enrichment of tobacco fields. Although it is well known that tobacco leaves may accumulate Cd (Lugon-Moulin et al., 2006), we emphasize that it was not the purpose of this study to assess the impact of Cd-containing P fertilizers on the Cd content of tobacco.

2. METHODS

Sampling: A total of 36 phosphate fertilizers were sampled in Africa, Asia, Europe and South America; namely in Austria (1), Brazil (6), China (3), the former Yugoslav Republic of Macedonia (FYROM) (2), Germany (1), Greece (12), India (1), Malawi (1), Mozambique (1), Tanzania (1), Thailand (1), Turkey (4) and Vietnam (2). Fertilizers were sampled in triplicate (from different fertilizer bags) except for the single samples in Austria, Germany, Mozambique and Thailand. Fertilizers from Malawi and Mozambique were the same (i.e. the same manufacturer and same formulation; phosphate rock origin not obtained). In the countries sampled, these fertilizers could well be applied on tobacco as well as on other crops. These same fertilizers may also be used for production of tobacco and other crops in other countries. Our sample size may appear small. However, the study aimed uniquely at pointing out whether some fertilizers may pose a potential problem for Cd field enrichment and whether others may pose less potential problems.

The fertilizers belonged to the following types: monoammonium phosphate (MAP), diammonium phosphate (DAP), single superphosphate (SSP), triple superphosphate (TSP), and compound fertilizers with various amounts of N, P and K. The latter included NP, PK and P-only fertilizers (the latter classified here as compound fertilizer). Some fertilizers contained additional nutrients such as boron (B), iron (Fe), magnesium (Mg) or sulfur (S). It is noted that many fertilizers with different formulations may be used for tobacco production. However, it was beyond the scope of this study to exhaustively represent all different P fertilizers that may be used in tobacco fields.

All sub-samples were digested by nitric and sulfuric acids (HNO₃ + H₂SO₄) using method 3.1.1 from the European Union. Total Cd was measured by graphite-furnace atomic absorption spectrometry (AAS). The P content was determined using method 3.2 from the European Union (gravimetric method using quinoline phosphomolybdate). P was expressed as % phosphorus pentoxide (P₂O₅). In addition, two samples with Cd concentrations at the upper range of the Cd distribution were analyzed for diethylenetriaminepentaacetate (DTPA)-extractable Cd to obtain an estimate of bioavailable Cd following the method of Lindsay and Novell (1978). All samples were sent to an external laboratory (AgroLab Swiss GmbH, Switzerland) for analyses. Cd concentrations were expressed both as mg Cd/kg fertilizer (i.e. on a part per million, ppm basis) and as g Cd/t P₂O₅ (Tab. I).

3. RESULTS AND DISCUSSION

Cd concentration in the fertilizers ranged from 0.08 ± 0.14 to 97.50 ± 8.74 g Cd/t P₂O₅ (Tab. I). The concentration given on a mg/kg basis was correlated with that given on a P₂O₅ basis (correlation coefficient \( r = 0.83; n = 100 \); four samples with total Cd reported as “<0.012 mg/kg” were attributed a concentration of 0.00 mg/kg for calculation purposes), but obvious discrepancies were noticed when there were large differences in P₂O₅ content (Tab. I). For example, a NPK fertilizer with a P₂O₅ content of 10% had 3.66 mg Cd/kg, which translated into 36.68 g Cd/t P₂O₅, whereas a P fertilizer with 46% P₂O₅ had a Cd concentration 2.5 times higher on a mg/kg basis (8.98 mg/g), but a ca. two-fold lower concentration on a P₂O₅ basis (19.55 g Cd/t P₂O₅).

The Cd concentration measured on a mg/kg basis was weakly correlated with the P₂O₅ content (correlation coefficient, \( r = 0.37; n = 100 \); four samples with total Cd reported as “<0.012 mg/kg” were attributed a concentration of 0.00 mg/kg for calculation purposes) because different phosphate rocks used in the fertilizer manufacturing can have different Cd concentrations (Van Kauwenbergh, 2002). Therefore, the phosphate rock origins of the fertilizers analyzed in this study were determined, when possible, and put in relation to the Cd content of the fertilizer. For discussion purposes, fertilizers were separated into three classes corresponding to the proposed limits to be gradually phased in by the European Union (EU); that is, limits of 60, 40 and 20 g Cd/t P₂O₅ (Hutton and de Meëts, 2001). Other limits exist or have been proposed (e.g. see Van Kauwenbergh, 2002), but it is not the purpose of the present study to discuss them.

Most fertilizers had < 20 g Cd/t P₂O₅ (55.6%; Tab. I). Some had a very low Cd content (about 1 g Cd/t P₂O₅), like the fertilizer manufactured using rock from the Kola Peninsula (Russia), and the one manufactured with phosphate rock from central Finland (+ 10% from Kola Peninsula). These two phosphate rocks originated from igneous phosphate deposits, which usually contain lower amounts of Cd than sedimentary phosphate deposits (Van Kauwenbergh, 1997, 2002). A phosphate rock sample from Finland (Siilinjarvi) had <2 mg Cd/kg while samples from the Kola Peninsula had Cd concentrations ranging from 0.3 to 2 mg/kg (Van Kauwenbergh, 2002). The two fertilizers sampled in Vietnam both had low Cd levels (<5 g Cd/t P₂O₅). For one of them, the phosphate rock originated from the Lao Cai quarry, the largest phosphate rock deposit in Vietnam. A fertilizer made from phosphate rock originating from Kaiyang (Guizhou province), a large phosphorus mine in China, contained 18.83 g Cd/t P₂O₅. Low Cd was reported in the sedimentary phosphate rock from the Kaiyang deposit, although it was based on a single sample (<2 mg/kg; Van Kauwenbergh, 2002). The fertilizers for which no information was available on the phosphate rock origin all fell under the limit of 20 g Cd/t P₂O₅. Moreover, two fertilizers made from phosphate rocks from Algeria and/or Tunisia fell into this class,
although deposits from North Africa may contain high Cd levels. Indeed, an average Cd concentration of 39.5 mg/kg (range: 30–56 mg/kg, n = 4) was reported for phosphate rocks from mines in Tunisia, and Cd ranged from 12 to 32 mg Cd/kg (n = 3) for Algerian deposits (Van Kauwenbergh, 2002). However, one of these two fertilizers (number 5 in Tab. I) showed a fairly large variation between replicates. Two sub-samples had essentially no Cd (<0.012 mg/kg), while the third one had 8.34 mg Cd/kg, i.e. 43.10 g Cd/t P₂O₅. Moreover, another fertilizer made from phosphate rock from Tunisia had 50.97 Cd/t P₂O₅.

A total of 29 fertilizers (80.6%) were under the limit of 40 g Cd/t P₂O₅, which included two fertilizers made from rock.
from Russia, although the exact deposit location was not obtained (Tab. 1). All fertilizers made from Syrian phosphate had < 40 g Cd/t P₂O₅. A phosphate rock sample from Syria (Khneifiss deposit) contained 3 mg Cd/kg (Van Kauwenbergh, 2002).

The majority of the fertilizers analyzed here had < 60 g Cd/t P₂O₅ (91.7%). Some were close to this limit, like the fertilizer made from phosphate rock from Jordan (59.89 g Cd/t P₂O₅). Phosphate rock analyzed from this country yielded from 3 to 12 mg Cd/kg (Van Kauwenbergh, 2002). The fertilizer made from phosphate rock originating from the Negev desert in Israel also had a relatively high Cd content (57.76 g Cd/t P₂O₅), which appears consistent with the reporting of an average Cd concentration of 30.77 mg/kg for this region (Van Kauwenbergh, 2002).

Only three fertilizers had a Cd concentration over the limit of 60 g Cd/t P₂O₅ (8.3%). The phosphate rock used to manufacture these “high-Cd” fertilizers originated from Khouribga (Morocco) and Central Florida (USA). Cd concentrations reported in phosphate rock from the mine of Khouribga ranged from 3–27 mg/kg (average: 15.06 mg/kg; n = 10), and those from central Florida, 3–20 mg/kg (average: 9.13 mg/kg; n = 27) (Van Kauwenbergh, 2002).

The fertilizer with the highest reported concentration (97.50 g Cd/t P₂O₅) was a MAP fertilizer whose phosphate rock was from Central Florida (Tab. 1). Interestingly, another MAP with the same formulation and sampled in the same country, but differing in the phosphate rock origin (Peninsula of Kola, Russia), had only 0.27 g Cd/t P₂O₅ (Tab. 1). This large (361 times) difference obtained for two fertilizers of the same type and formulation and commercialized in the same country suggests that the screening of fertilizers’ sources to avoid “high-Cd” fertilizers may contribute to avoiding further Cd soil contamination.

The potentially bioavailable fraction of Cd in two fertilizers containing relatively high levels of Cd was estimated (Tab. 1). In both cases, > 50% of the total Cd was extractable by DTPA (50.3% and 65%, respectively), therefore both have considerable potential bioavailability. However, it is not known to what extent the Cd added to the fields through the fertilizers analyzed in this study might have been available for uptake by tobacco. Cd availability to the plant may be affected by complex genotype X environment interactions, the study of which was beyond the scope of this work. Few studies on the transfer efficiency of Cd from fertilizers to plants under field conditions are reported in the literature (Huang et al., 2004). Some studies suggest that P fertilizer application may increase the Cd concentrations in tobacco leaves (Miele et al., 2002; Semu and Singh, 1996; reviewed in Lugon-Moulin et al., 2004), but different fertilizers, though having a similar Cd content, may have different impacts on the final concentration in the tobacco leaves. For example, the use of fertilizers with different N forms can lead to significant differences in the Cd concentration in tobacco leaves (Phu Lich et al., 1990; Tsadilas et al., 2005). Furthermore, as tobacco is subdivided into many different cultivars, and is cultivated worldwide on different soils and under different agro-climatic conditions, the availability to tobacco of Cd added through fertilizers may vary depending on various conditions. It is indeed known that various factors such as soil pH may affect Cd uptake by tobacco (Lugon-Moulin et al., 2004; Tsadilas et al., 2005).

4. CONCLUSION

By sampling fertilizers in various countries and continents, we showed that the range of Cd concentration in phosphate fertilizers used for tobacco production varies considerably, despite our limited sample size. A more extensive sampling of Cd and P concentration in phosphate rock deposits and in the fertilizers made from such deposits, also taking into account the manufacturing process, would be needed to obtain a comprehensive picture of the Cd concentration and its variability in such deposits and fertilizer samples. Nevertheless, fertilizers appear to be one of the sources that can contribute to adding new Cd to agricultural soil. These additions can be controlled/prevented to some extent, by selecting the use of “low” Cd-containing fertilizers in tobacco production.

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