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Accumulation of cadmium and uranium in arable soils in Switzerland[☆]

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ABSTRACT

Mineral phosphorus (P) fertilizers contain contaminants that are potentially hazardous to humans and the environment. Frequent mineral P fertilizer applications can cause heavy metals to accumulate and reach undesirable concentrations in agricultural soils. There is particular concern about Cadmium (Cd) and Uranium (U) accumulation because these metals are toxic and can endanger soil fertility, leach into groundwater, and be taken up by crops. We determined total Cd and U concentrations in more than 400 topsoil and subsoil samples obtained from 216 agricultural sites across Switzerland. We also investigated temporal changes in Cd and U concentrations since 1985 in soil at six selected Swiss national soil monitoring network sites. The mean U concentrations were 16% higher in arable topsoil than in grassland topsoil. The Cd concentrations in arable and grassland soils did not differ, which we attribute to soil management practices and Cd sources other than mineral P fertilizers masking Cd inputs from mineral P fertilizers. The mean Cd and U concentrations were 58% and 9% higher, respectively, in arable topsoil than in arable subsoil, indicating that significant Cd and U inputs to arable soils occurred in the past. Geochemical mass balances confirmed this, indicating an accumulation of 52% for Cd and 6% for U. Only minor temporal changes were found in the Cd concentrations in topsoil from the six soil-monitoring sites, but U concentrations in topsoil from three sites had significantly increased since 1985. Sewage sludge and atmospheric deposition were previously important sources of Cd to agricultural soils, but today mineral P fertilizers are the dominant sources of Cd and U. Future Cd and U inputs to agricultural soils may be reduced by using optimized management practices, establishing U threshold values for mineral P fertilizers and soils, effectively enforcing threshold values, and developing and using clean recycled P fertilizers.

1. Introduction

Phosphate (P)-containing mineral fertilizers contain trace elements that are potentially hazardous to humans and the environment (Kratz et al., 2016; McLaughlin et al., 1996; Schnug and Lottermoser, 2013). Agricultural productivity and ecosystem services can be negatively affected by the use of phosphate-containing fertilizers because of the undesirable amounts of heavy metals added to soil in the fertilizers (Mar and Okazaki, 2012). Metals that are mobile and available to plants may be transferred to crops, groundwater, and surface water (McLaughlin et al., 1996; Schnug and Lottermoser, 2013; Wilcke and Döhler, 1995). Cadmium (Cd) and Uranium (U) may be important impurities in mineral P fertilizers, and there is particular concern about these metals being added to soil in fertilizer because they are toxic (Camelo et al., 1997; Mar and Okazaki, 2012; McLaughlin et al., 1996). Heavy metal concentrations in mineral P fertilizers vary widely depending on the origins of the phosphate rocks used to produce the fertilizers and the nature of the finished fertilizers. For example, Cd concentrations (per kilogram of P) from 1 to >640 mg kg^{-1} have been found in fertilizers (McLaughlin et al., 1996; Ulrich et al., 2014). Phosphate rocks are relatively insoluble in water, so they are processed to make fertilizers. Radionuclides and heavy metals become concentrated during these processes, and can reach 1.5 times the concentrations found in the unprocessed ore (Sattouf, 2007).

The problem of Cd in fertilizers accumulating in soils has been

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investigated in a number of studies in Sweden (Bengtsson et al., 2003), Germany (Boyson, 1992; Knappe et al., 2008; Wilcke and Döhler, 1995), the Netherlands (Moolenaar and Lexmond, 1998), England and Wales (Nicholson et al., 2003), Australia (Mann et al., 2002), New Zealand (Gray et al., 1999; Schipper et al., 2011) and its general implications for soil, environmental and human health (de Vries et al., 2005; Moolenaar et al., 1997; Oborn et al., 2003) and plant uptake (Johnston and Jones, 1992) were assessed. It is well known that Cd in fertilizers can accumulate in agricultural topsoils and that the amount that accumulates depends on the fertilization rate, the crop rotation used, and the properties of the soil (Mann et al., 2002; McLaughlin et al., 1996). Mineral P fertilizer is the main source of Cd to a soil if the fertilizer is applied regularly (Keller and Schulin, 2003; Moolenaar and Lexmond, 1998). Cd is also added to soil by the application of manure and atmospheric deposition (Nicholson et al., 2003). In the past, the application of sewage sludge may also have added Cd to soil (Kabata-Pendias and Mukherjee, 2007; Keller et al., 2005), but applying sewage sludge to soil is now prohibited in many countries, and was prohibited in Switzerland in 2006. Cd is predominantly removed from soil through the harvesting of crops and, depending on the properties of the soil, the leaching of Cd to deeper soil layers. It has recently been found that current Cd soil budgets in the European Union and Norway are almost in balance (Six and Smolders, 2014). These authors suggested that Cd concentrations in soils will decrease over the next few decades. However, this conclusion was based on average values for Europe, and Cd concentrations in soils will not necessarily decrease in areas with particular crop rotations and fertilization regimes.

Relatively little information is available on the behaviour of U in soils derived from P fertilizers. U may become enriched in topsoils (Takeda et al., 2006; Wetterlind et al., 2012) but can be mobile and leach into groundwater and surface water (Schnug and Lottermoser, 2013; Schnug et al., 2005; Iurian et al., 2015). Mineral P fertilizer is the main source of U to agricultural soils, and manure or sewage sludge application and atmospheric deposition are minor sources (Bottcher et al., 2012; Kabata-Pendias and Mukherjee, 2007; Kratz et al., 2008). Kratz et al. (2008) found that U inputs from manure or sewage sludge are 13%–45% of U inputs in mineral P fertilizers containing the same amounts of P. Plants take up relatively little U from soil, but U in soil can sorb to roots and enter the food chain in root vegetables (ATSDR, 2013; Kratz et al., 2008). However, humans ingest negligible amounts of U in plant products, and it has been suggested that drinking water is the main source of human U uptake (Schnug and Lottermoser, 2013; Schnug et al., 2005). While some studies stated that concentrations of U in drinking water vary regionally and are generally related to the geological bedrock (CCME, 2011; Stalder et al., 2012), other studies found that (depending on soil properties) fertilizer derived U will not significantly accumulate in soils, but is readily transferred to aquifers (Birke and Rauch, 2008; Huhle et al., 2008; Smidt et al., 2012).

A number of factors, listed below together with their trends, need to be considered when assessing the importance of mineral P fertilizers in the accumulation of Cd and U in agricultural soils.

1. As in many European countries the amount of mineral P fertilizer used has decreased significantly since the 1990s in Switzerland (Spiess, 2011). For instance, 16562 t of mineral P fertilizer was applied to agricultural land in Switzerland in 1990, reducing to 4206 t in 2013 (BLW, 2014).
2. Mineral P fertilizers are predominantly applied where crops with high P demands are grown and insufficient animal manure is available to meet the P demands of the crops.
3. Several mineral P fertilizers contain high concentrations of Cd and U (Gisler and Schwab, 2015; Nziguheba and Smolders, 2008). In a recent Swiss survey, 45% of all the mineral P fertilizers analysed contained Cd concentrations higher than the Swiss threshold (50 mg kg^{-1} P), and the highest concentration was 220 mg kg^{-1} (Gisler and Schwab, 2015). No thresholds for U in fertilizers have yet been set. Swiss fertilizers have been found to have relatively high median and maximum U concentrations, of 291 and 485 mg kg^{-1} P_2O_5, respectively (Gisler and Schwab, 2015).

In two recent studies, FitzGerald and Roth (2015) and Roth and FitzGerald (2015) concluded that Cd concentrations in the fertilizers used in Switzerland need to be as low as possible because some sections of the population already have Cd intakes close to the tolerable daily intake. They also concluded, because of the toxicity of U, that U concentrations in fertilizers should be more closely monitored than they are currently. Better information on the fates of Cd and U in mineral fertilizers added to soils is needed than is currently available because such information will be required to allow rational debates about managing fertilizer quality in Switzerland and achieving long-term decreases in risks caused by agricultural activities.

In the study described here, we compared Cd and U concentrations in topsoil samples from agricultural and grassland sites and in topsoil samples and subsoil layers (C horizon) at agricultural sites. The aim was to determine whether Cd and U have accumulated in topsoils at arable sites compared to topsoils at grassland sites to which smaller amounts or no mineral P fertilizers have been added. In a second trial, topsoils of arable sites were compared to deeper soil layers at the same sites, to assess Cd and U accumulation by input from the surface. We also determined Cd and U concentrations in archived soil samples from selected soil monitoring sites in Switzerland that have, in the past, received regular mineral P fertilizer, and calculated Cd and U budgets for the sites over a 25-year period. The aim of the study was to attempt to answer the following questions.

I. Are higher Cd and U concentrations found in arable soils than in grassland soils to which little or no mineral fertilizer has been applied?
II. Are Cd and U more enriched in arable topsoils than in subsoils?
III. What are the main sources of Cd and U to the arable soils, and are Cd and U still being accumulated appreciably?
IV. What political measures should be taken to decrease Cd and U inputs to soils from mineral P fertilizers?

2. Materials and methods

2.1. Study sites

Cd and U concentrations in about 400 archived soil samples from Switzerland were determined. The samples were from 216 agricultural sites in areas in which mineral P fertilizers are used on arable land. The sites were chosen using georeferenced farm census data that allowed areas containing arable farms to be identified (Fig. 1 and Fig. S1). Arable farms do not generally have access to sufficient animal manure to provide the nutrients required by arable crops, so we presumed that mineral P fertilizers are predominantly applied on arable farms. Archived soil samples were available from the Swiss soil monitoring network (NABO; from which soil samples collected from 34 arable sites between 2005 and 2009 were available), the Swiss biodiversity monitoring