Science of the Total Environment 926 (2024) 171482

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Cadmium, zinc, and copper leaching rates determined in large monolith lysimeters

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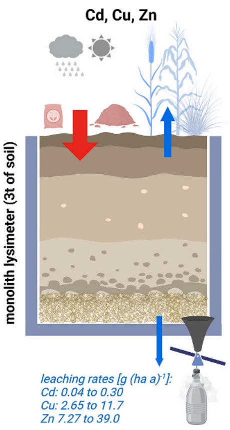
HIGHLIGHTS

- A lysimeter facility was used to determine leaching rates of Cd, Cu, and Zn
- Cd, Cu, Zn leaching rates were small and had a minor impact on soil mass balances
- Leaching models seem to overestimate leaching rates
- Direct transfer of Cd, Cu, Zn from the soil surface out of the soil profile was small

GRAPHICAL ABSTRACT



ARTICLE INFO

Editor: Paola Verlicchi

Keywords:
Seepage water
Crops
Soil mass balances
Isotope tracing
Crop rotation
Arable soils

ABSTRACT

Soil mass balances are used to assess the risk of trace metals that are inadvertently applied with fertilizers into agroecosystems. The accuracy of such balances is limited by leaching rates, as they are difficult to measure. Here, we used monolith lysimeters to precisely determine Cd, Cu, and Zn leaching rates in 2021 and 2022. The large lysimeters ($n = 12$, 1 m diameter, 1.35 m depth) included one soil type (cambisol, weakly acidic) and distinct cropping systems with three experimental replicates. Stable isotope tracers were applied to determine the direct transfer of these trace metals from the soil surface into the seepage water. The annual leaching rates ranged from 0.04 to 0.30 for Cd, 2.65 to 11.7 for Cu, and 7.27 to 39.0 g (ha a)$^{-1}$ for Zn. These leaching rates were up to four times higher in the year with several heavy rain periods compared to the dry year. Monthly resolved data revealed that distinct climatic conditions in combination with crop development have a strong impact on trace metal leaching rates. In contrast, fertilization strategy (e.g., conventional vs. organic) had a minor effect on leaching rates. Trace metal leaching rates were up to 10 times smaller than fertilizer inputs and had therefore a minor impact on soil mass balances. This was further confirmed with isotope source tracing that showed that

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https://doi.org/10.1016/j.scitotenv.2024.171482
Received 22 December 2023; Received in revised form 20 February 2024; Accepted 3 March 2024

only small fractions of Cd, Cu, and Zn were directly transferred from the soil surface to the leached seepage water within two years (< 0.07 %). A comparison with models that predict Cd leaching rates in the EU suggests that the models overestimate the Cd soil output with seepage water. Hence, monolith lysimeters can help to refine leaching models and thereby also soil mass balances that are used to assess the risk of trace metals inputs with fertilizers.

1. Introduction

In agriculture, fertilizers can be inadvertently the major input of trace metals into soils (Hou et al., 2020). For instance, mineral phosphorus fertilizers can be enriched in cadmium (Cd) compared to soils and crops, since phosphate rocks can be concentrated in Cd (Mar and Okazaki, 2012). Hence, mineral P fertilizer can contribute to increased Cd concentrations in soils and crops in the long-term (Bergen et al., 2021; Grant et al., 2013; Hu et al., 2024). In crops, Cd concentration should be kept to a minimum since Cd has along half-life time in human bodies, and can damage organs such as the kidney and is considered as a class 1 carcinogen (Fransson et al., 2014; Godt et al., 2006; WHO/IARC, 2020). Moreover, organic fertilizer can contain high concentrations of copper (Cu) and zinc (Zn) through the use of these trace metals as growth promoter in animal production systems such as for pigs (Brugger and Windisch, 2015; Formentini et al., 2015). Although Zn and Cu are essential nutrients for soil biota and plants, an excessive accumulation of these elements can impair soil functions (Mertens and Smolders, 2013; Rehman et al., 2019). Hence, excessive inputs of fertilizers with high trace metal concentrations can pose a health and/or an environmental risk.

To assess the risk of trace metal inputs from fertilizers into soils, soil mass balance models are used (Marini et al., 2020). These balances take into account soil in- and outputs to determine if there is a net accumulation of trace metals (Gross et al., 2021; Shi et al., 2018). Based on the accumulation rate of trace metals, it can be assessed if the current agricultural practices impair soil fertility and crop quality in the mid and long-term. Currently, the largest uncertainty in the soil mass balances modelling of trace metals are outputs with seepage water (Six and Smolders, 2014). This issue has been particularly discussed for Cd, as recent publications reviewed that modelled leaching rates exceed measured leaching rates by 2 to 250 times (McLaughlin et al., 2020; Sterckeman et al., 2018). Hence, either modelled Cd leaching rates underestimate and/or measured leaching rates overestimate soil Cd accumulation. This disagreement introduces uncertainties into soil mass balances and thereby complicates risk assessments and political debates on Cd limits in fertilizers (Dharma-wardana, 2018; Ulrich, 2019). Hence, precise Cd leaching rates are needed to assess the risk of Cd inputs with fertilizers into soils.

From all in- and output fluxes, trace metal leaching rates are the most difficult ones to measure. The methods used to measure trace metal leaching rates include suction cups, wick samplers, and lysimeter techniques (Bengtsson et al., 2006; Cambier et al., 2014; Degryse and Smolders, 2006; Filipović et al., 2016; Gray and McDowell, 2016; Gray and Cavanagh, 2021; Imseng et al., 2018; Keller et al., 2002; McLaren et al., 2004). All these methods have advantages and disadvantages (Weihermüller et al., 2007). For instance, suction cups and wick samples are easier to install than lysimeter-based methods (Meissner et al., 2014; Weihermüller et al., 2007). However, they mostly rely on modelling of water fluxes and provide a small surface area to collect the seepage water. Hence, they may not fully account for small scale heterogeneities and preferential-flow pathways in soils (Li and Zhou, 2010; Weihermüller et al., 2007). In addition, suction cups may also filter trace metals that are associated with colloids. Lysimeter typically consist of a container filled with soil and a device to collect the water outflow of the container to determine seepage volumes and leaching rates of nutrients and pollutants (Meissner et al., 2016). Large lysimeters with soil monoliths (i.e. undisturbed soils) account for preferential flow pathways and average small scale heterogeneities of soils (Germann and Prasuhn, 2018; Meissner et al., 2014). Therefore, lysimeters directly and precisely assess seepage water fluxes and elemental fluxes (Meissner et al., 2014; Weihermüller et al., 2007). However, most of these large lysimeters are free draining, thereby, the bottom is in contact with atmospheric pressure which can introduce artifacts in the water flow (Weihermüller et al., 2007). Nevertheless, as large and monolithic lysimeter solve most challenges of seepage water measurements, they provide a system that represents real field conditions most realistically (Meissner et al., 2014). To date, only a few studies have used large and monolithic lysimeter to determine trace metal leaching rates in grassland soils (Gray et al., 2021; Keller et al., 2002; McLaren et al., 2004). To account for other agricultural systems such as arable crops, different fertilization strategies, and soil types, more studies are needed that determine precise trace metal leaching rates with large and monolithic lysimeters.

Isotope source tracing allows to distinguish trace metal sources (e.g. fertilizers, soils) and sinks (e.g., plants, soil pools, and seepage water) (Bracher et al., 2021; Hippler et al., 2015; McBeath et al., 2013; Ostermann et al., 2015). In addition, enriched stable isotope source tracing techniques allow to precisely trace the fate of the fertilizer applied trace metals over several growing seasons (Mattiello et al., 2021). For instance, pot experiments revealed that only a small fraction of the trace metals that are applied with mineral and organic fertilizers are directly transferred to the crops (< 12 %, Bracher et al., 2021; Künzli et al., 2023; Yan et al., 2021). Hence, the majority of the trace metals (> 88 %) remained in the soil and/or could be leached out of the soil profile with seepage water (Bracher et al., 2021; Ostermann et al., 2015). To date, the direct transfer of fertilizer applied Cd, Cu, and Zn to crops and seepage water that is leached out of the soil profile has not been quantified. Such a source tracing study would provide novel insights into the fate of fertilizer applied metals.

The objectives of this study were to i) determine leaching rates of Cd, Cu, and Zn of distinct cropping systems and to ii) quantify the direct transfer of these trace metals from the lysimeter surface to the seepage water. To this end, we conducted an experiment at the state-of-the-art lysimeter facility at Agroscope Zurich-Reckenholz, Switzerland. The experiment included 12 monolith lysimeters that contained each three tons of soil as well as four treatments with distinct cropping systems that differed in their fertilization strategy and crop rotation. Each treatment contained three experimental replicates and one weighable lysimeter. For one treatment, a stable Cd, Cu, and Zn isotope source tracing experiment was conducted. The obtained leaching rates and soil mass balances are discussed in the context of the risk of fertilizer applied trace metals.

2. Material & methods

2.1. Lysimeter facility and experimental design

The lysimeter facility at Agroscope in Zurich-Reckenholz comprises 72 monolith lysimeters (Prasuhn, 2016). The monolith lysimeters have a surface area of 1 m^2, a depth of 1.5 m and are kept in stainless steel containers (steel type DIN V2A 1.430, main metallic components Cr and Ni). The top 1.35 m are soil monoliths (i.e. undisturbed soil) while the lowest 0.15 m are composed of three layers of quartz sand and gravel that contain small quartz grains on top (0.10 to 0.50 mm) and the largest ones at the bottom (3.15 to 5.60 mm). The latter is used to minimize the disruption of the water flux from the soil monolith to the exposure of atmospheric pressure at the bottom of the monolith (Abdou and Flury, 2004; Meissner et al., 2014). At the bottom of the lysimeter, the seepage water is directed to a tipping bucket that tips over every 100 mL accumulated. The time of each tipping is recorded. Precipitation rates are measured using a national meteorological station of MeteoSwiss located 50 m aside from the lysimeter facility. The evapotranspiration is calculated based on the measured precipitation, seepage water rates, and the change of stored water in the lysimeter (see SI 1.1).

For this study, 12 out of the 72 lysimeters have been selected. The soil of the selected lysimeters was an arable soil from the Swiss Plateau from Grafenried (canton Bern) and was classified as a "slightly pseudogleyed cambisol" (Table S1). The 12 lysimeters encompass four different treatments with $n = 3$ experimental replicates. Since 2009, the treatments have been fertilized differently (Table S2). The 'conventional' and the N100 treatment have been fertilized according to recommendations of Agroscope, while the N200 treatment received higher N application rates than recommended (Sinaj and Richner, 2017). These treatments have been chosen when the lysimeters were installed in 2009 to focus on nitrate leaching in agriculture (Prasuhn, 2016). The 'organic' treatment has been managed according to organic farming practices without pesticides and chemically treated mineral fertilizers. In the conventional and organic treatment, winter barley was grown in 2021 followed by a multi-annual temporary grass-clover ley (denoted as grass-clover ley) that was sown in August and kept until the end of the sampling campaign of this study. In the N100 and N200 treatments, silage maize was grown in 2021 and 2022 with a green manure crop in between. Each treatment contained one weighable lysimeter (± 10 g) and two lysimeters that were not weighable (Prasuhn, 2016). Taken together, the lysimeter system used here can be classified as a large, weighable, free draining, and monolith lysimeter (Meissner et al., 2010).

2.2. Sampling and sample processing for concentration measurements

Samples were taken from November 2020 to October 2022. To this end, seepage water samples were collected in 25 L polyethylene (PE) canisters that were pre-cleaned with 0.03 M double distilled nitric acid (HNO_3). The sampling was regularly conducted monthly or bi- to tri-monthly when the canisters filled too quickly. The canisters were collected, replaced with empty ones (also acid cleaned), and transported to the Research Station of Plant Sciences at ETH. There, the seepage water was acidified with double distilled HNO_3 to decrease the pH below 3 to ensure that Cd, Zn, and Cu desorbed from potential binding sites of the canisters. After adding the acid, the canisters were shaken to homogenize the seepage water. This was necessary, as sometimes, there were small soil particles visible in the seepage water, particularly after heavy rainfalls or snow melting periods.

Before an aliquot was taken, the canisters were again shaken. Then, 200 mL of the homogenized seepage water was evaporated at 120 °C in a laminar fume hood. The air that circulated through the hood was filtered and the hood was constructed with plastic material only to minimize contamination of the samples with metals. The evaporated samples were then resuspended in 0.3 M HNO_3 at 100 °C on the hotplate for 1.5 h. After this, the samples were transferred into polypropylene tubes (VWR, Sterile Metal-Free Centrifuge Tubes) and precisely filled up to 15 mL. For each batch of samples that was processed, a blank consisting of ultrapure water (> 18.2 MΩ) was processed alongside the normal samples to later determine the quantity of trace metals that were added to the samples during sample processing. Finally, the samples were stored in a fridge at 4 °C temperature until they were measured.

Plant and fertilizer samples were frequently taken upon harvest or application and then air dried in an oven (50 °C). Data on harvested biomass (g m^{-2}) and fertilizer application rates (g m^{-2}) were recorded. Harvested biomass and fertilizers were homogenized using a rotary mill equipped with tungsten carbide cups (Quiagen, TissueLyzer). Note, the plants were treated as aboveground biomass, thereby, grains, stems, and leaves were not separated as we were only interested in the metal export from the soil with the harvested biomass. The plant and mineral fertilizer samples were then digested using 7 M double distilled HNO_3 and a single reaction chamber microwave system (turboWave, MWS microwave systems) (Künzli et al., 2023). The organic fertilizers (that were applied to the lysimeters as liquid slurries) were shaken and an aliquot was taken with a pipette. The aliquot was then digested with 7 M HNO_3 in the microwave as done for the mineral fertilizers and the plants. For the digestions, blanks and certified standard materials were processed alongside the samples.

Soil characterization was conducted previously when the lysimeters were installed. For this publication, metal related soil properties were additionally measured. As it was not possible to destructively sample soil from the lysimeter, the trace metal related soil properties were determined in a mixed soil sample that included all soil horizons and that was sampled when the soil was transferred to the lysimeter facilities in 2009. In this soil sample, total metal concentrations were determined by using a mix of HNO_3, HCl, and HF (Kersten et al., 2022). DTPA extractable metals were conducted following the protocol of Lindsay and Norvell (1978). All soil properties are summarized in Table S1.

2.3. Concentration analyses and quality control

The concentrations of Cd, Cu, and Zn in seepage water, plant, soil, and fertilizer samples were analyzed using an inductively coupled plasma mass spectrometer with a helium supplied reaction cell (ICP-MS, Agilent 7500ce). To this end, the isotopes ^{111}Cd, ^{63}Cu, and ^{66}Zn were measured and corrected for matrix induced sensitivity effects with the internal standards scandium (Cu, Zn) and indium (Cd) (Thomas, 2013).

Several quality control samples were integrated into the concentration measurements. For seepage water samples, the accuracy of the analyzes was tested with the certified reference material CRM-CA713 (wastewater, $n = 1$). The recoveries ranged from 110 to 113 % for Cd, Cu, and Zn which indicates a slight overestimation of our results. Repeat measurements of seepage water samples ($n = 7$) revealed a relative standard deviation of 3 to 6 % for Cu and Zn and 9 % of Cd. The precision of Cd was likely smaller compared to Cu and Zn because of the low concentration of the Cd samples. Nevertheless, the quality control measurements revealed that the accuracy and precision of liquid samples were adequate. In addition, the procedural blanks of the seepage water samples were 0.001 μg L^{-1} for Cd, 0.02 μg L^{-1} for Cu, and 0.5 μg L^{-1} for Zn (of $n = 5$). For Cd and Cu, the average contributions of the procedural blanks to the seepage water samples were below 3 %. For Zn, the average contribution of the procedural blanks ranged from 8 to 20 %. The higher blank contribution is typical for Zn as it is present in many laboratory materials (Garçon et al., 2017). To ensure that the results were not overestimated, the blank concentrations were subtracted from the concentrations obtained in the seepage water samples for Cd, Cu, and Zn.

Quality control samples were also measured for plant samples. The recoveries of the standards BCR-679 (white cabbage), NIST 1567b (wheat flour) and IAEA-V10 (hay powder) ranged from 96 to 100 % for Cd, 89–90 % for Cu, and 89 to 93 % for Zn. These results indicated that the quality of sample processing (milling, digesting) and analyses for plant samples were robust.

2.4. Isotope labeling and isotope analyses

In November 2020, ^{111}Cd, ^{65}Cu, and ^{67}Zn enriched stable isotope spikes were added to the conventional treatment where winter barley has just been sown. The abundances of the enriched isotopes were ^{111}Cd = 95 %, ^{65}Cu = 99 %, and ^{67}Zn = 91 %. The quantity added of each metal was calculated based on Cd, Cu, and Zn contents and application rates of P-fertilizers in Swiss agriculture (Sinaj and Richner, 2017; Gisler and Schwab, 2015) which resulted in an application rate of 5 g Cd, 8 g Cu, and 30 g Zn per ha. Hence, the form (i.e. soluble) and quantity of the spike applied was to mimic a representative soluble and mineral P fertilizer. To apply the enriched stable isotopes to the lysimeters, the stock solution was diluted in a plastic watering can to a volume of 2 L. Then, we added the isotope spike solution evenly in between the eight inner barley rows (total 10 rows) to minimize boarder effects.

To measure the enriched stable isotope ratios in the sinks (i.e. seepage water and plants) required additional sample treatment. For the seepage water, aliquots of the samples were bulked to nine periods to ensure that isotope ratios could be adequately measured. Typically, one period was equal to three months. For the plants, samples were homogenized and digested using a microwave system (see details in Section 2.2). To increase the precision of the isotope ratio measurements and to concentrate the samples, the samples were purified (Dürr-Auster et al., 2019). To this end, the samples were evaporated to complete dryness, redissolved in HCl, and then the matrix elements (i.e. major cations such Ca and Mg) were separated from Cd, Cu, and Zn. Particularly, samples were loaded in 7 M HCl (5 mL) to preconditioned resin-based anion exchange chromatography resins (AG® 1-X8, 100–200 mesh, chloride form, Bio-Rad laboratories). The sample matrix was eluted using 7 M HCl (3 mL). After this, Cd, Cu, and Zn were eluted using H_2O (2 mL) and 0.3 M HNO_3 (8 mL). The samples were then evaporated to complete dryness, and redissolved in 0.3 M HNO_3. Note, a full recovery of the Cd, Cu, and Zn added to the columns was not a requirement as in isotope fractionation studies (Wiggenhauser et al., 2022) as the isotope fractionation induced during the purification is negligible in studies using enriched stable isotopes (Dürr-Auster et al., 2019). In addition, the concentrations of the samples were determined conventionally, as the changes in the isotope composition of these samples were too small to induce errors in the concentration measurements (see details in Künzli et al., 2023).

The isotope ratios ^{111}Cd: ^{110}Cd, ^{65}Cu: ^{63}Cu, and ^{67}Zn: ^{66}Zn in the purified samples were measured using a single collector ICP-MS (Dürr-Auster et al., 2019; Künzli et al., 2023). The integration time for the data acquisition was set to 1.5 s for Cd and 0.5 s for Cu and Zn. In addition, the ICP-MS was set to He mode (i.e. with collision cell) and isotope mode to increase the scans from 100 (concentration mode) to 1000 (isotope mode). The precision of the isotope ratio measurements was determined in replicate analyses of $n = 5$ samples. The relative standard deviation of the repeat analyses revealed that the isotope ratios could be resolved with a precision of 1.39 % for Cd, 0.18 % for Cu, and 0.29 % for Zn. This precision is typical for enriched stable isotope experiments measured with single collector ICP-MS (Stürup et al., 2008).

2.5. Calculations & Statistic

The leaching rates of trace metals from the soil were calculated as

$$Output_{spw} = concentration_{spw} \times seepage\ volume \tag{1}$$

where spw denotes seepage water, the concentration is expressed as μg L^{-1} and the seepage volume in L m^{-2}. The annual leaching rate was then calculated as the sum of all leaching rates per month. Outputs of trace metals with the harvests (i.e. crop harvest) were calculated as

$$Output_{crop} = concentration_{crop} \times harvest_{crop} \tag{2}$$

where the concentrations are expressed as mg (kg dry weight)$^{-1}$ and the harvest as g m^{-2}. Finally, inputs of trace metals with fertilizers were calculated as

$$Input_{fertilizer} = concentration_{fertilizer} \times application\ rate_{fertilizer} \tag{3}$$

where the concentration of the fertilizers is expressed as mg (kg dry weight)$^{-1}$. The application rate of the fertilizer is either expressed as g m^{-2} and L m^{-2}. For the annual soil mass balances, the in- and outputs were converted into the g ha^{-1}, and the soil mass balances were calculated as

$$Balance_{soil} = inputs - outputs \tag{4}$$

Thereby, a positive balance denotes a trace metal accumulation and a negative balance a depletion. Standard deviation for the seepage water and crops were calculated based on $n = 3$ experimental replicates. However, this approach was not possible for fertilizer inputs as the same fertilizer was applied to the three experimental replicates of the lysimeter. Hence, standard deviations were calculated based on the reproducibility that was determined with procedural replicates (processing + analyses). The standard deviation for the mass balance in Eq. (4) was calculated as

$$sd_{balance} = \sqrt{sd_{input}{}^2 + sd_{output}{}^2 + \dots} \tag{5}$$

where sd denotes the standard deviation of in- (fertilizers) and outputs (crop harvest, seepage water).

In the conventional treatment, the measured isotope ratios were used to calculate the recovery of the applied Cd, Cu, and Zn isotope spike in the seepage water and in the plant. In a first step, the fractions of Cd, Cu, and Zn that derived from the soil and from the spike were determined (McBeath et al., 2013):

$$f_{Cd\_spike} = \frac{NA_{110}{}^*IR_{seepage} - NA_{111}}{(SA_{111} - NA_{111}) - IR_{seepage}(SA_{110} - NA_{110})} \tag{6}$$

As exemplified for Cd, NA denotes the natural abundance of the mentioned isotopes according to IUPAC (Berglund and Wieser, 2011), and SA is the specific abundance of the isotopes in the spike. The $IR_{seepage}$ denotes the isotopic ratios ^{111}Cd:^{110}Cd in the seepage water samples. The results are expressed as fractions ranging between 0 and 1 (per time period chosen). The same equations can be used to calculate the fractions of Cu and Zn derived from the spike. In addition, 'seepage water' can be replaced by 'plant' to calculate the contribution of Cd, Cu, and Zn in the spike to the plant. Based on the fraction of Cd that derived from the Cd applied fertilizer in seepage water, the recovery of the Cd applied with fertilizer can be calculated:

$$Cd_{rec\_spike[\%]} = \frac{f_{Cd_{spike}}{}^*Cd_{seepage}}{Cd_{added}{}^*100}{}^*100 \tag{7}$$

where $Cd_{seepage}$ is the total Cd mass in the seepage water in g (ha and time period)$^{-1}$. Also here, the equation can be used to calculate the recovery of Cd, Cu, and Zn in seepage water and plants.

Significant differences of the mean among the different treatments were determined using a one-way ANOVA followed by a Tukey HSD test. These tests were applied for average Cd, Cu, and Zn concentrations in the seepage water and the corresponding leaching rates. Thereby, the level of significance was set to $p < 0.05$. Prior to the ANOVA, the equality of variances was tested using a Levene test and normal distribution of the residuals was tested using a visual inspection and a Shapiro Wilk test. If the prerequisites were not fulfilled, the data was either log10, square root, or 1/x transformed. All statistical analyses were conducted using the statistical software R (version 4.2.0).

3. Results

3.1. Water fluxes

The sampling years were characterized by exceptional and opposing climatic conditions. The annual rainfall was larger in the year 2021 (1001 mm) compared to 2022 (814 mm, Fig. S1a). The year 2021 was characterized by exceptionally wet, cool and low-radiation conditions. The rainfall anomaly in July 2021 amounted to over 90 % above the long-term average between 1991 and 2020, while potential evapotranspiration was 15 % lower than long-term-averages of this month (Figs. S1b, S2b). During the dry year 2022, precipitation anomalies were largely negative between January and August (Fig. S1b), while potential evapotranspiration was exceptionally high during this period (Fig. S2b). The distinct climatic conditions in 2021 and 2022 were mirrored in the seepage volume of the lysimeters. The annual seepage volume of the different treatments was about double in 2021 (472–562 mm or L m^{-2}) compared to the seepage volume in 2022 (214–227 L m^{-2}). In addition, the monthly seepage volume peaked in January and May–July 2021 up to 148 mm (Fig. 1). The seepage volumes in July were the highest recorded since the lysimeter facility has been running (2009). In contrast, the maximum monthly seepage volume in 2022 was 92 mm. Together, the two years of investigation can be characterized as a year with several heavy rain events and consequently high seepage volumes (2021) and a dry year with low seepage volumes (2022).

While the annual seepage volume between the different treatments were not distinguishable, the monthly seepage volume patterns differed substantially (Fig. 1). For instance, the seepage volume in May and June 2021 ranged from 75 to 100 mm $month^{-1}$ for the N fertilization treatments while the monthly seepage volume in the organic and conventional treatment were below 8 mm $month^{-1}$. These different seepage volumes corresponded with the actual evapotranspiration rates for each treatment (Fig. S2a). The evapotranspiration rates in May and June 2021 in the conventional and organic treatment (90 to 130 mm) were much higher compared to the N fertilization treatments (70 to 90 mm). In contrast, the actual evapotranspiration rates were much higher in the N100 and N200 fertilizer treatments (140 to 150 mm) compared to the conventional and organic treatment (30 to 50 mm) in July and August. This negative relationship between seepage volume and evapotranspiration corresponded with the timing of the biomass production of the different crops that grew in the different treatments. In the conventional and organic treatments, winter barley was grown and harvested in early July while in the N treatments, silage maize grew which reached peak biomass increase in July and August. Hence, the distinct crops in the different treatments strongly controlled the monthly seepage volumes in the monolith lysimeters.

3.2. Trace metal concentrations and leaching rates

The average Cd concentration in the seepage water ranged from 0.02 to 0.07 μg L^{-1} (Table S3). These low concentrations could be adequately measured through evaporation of the sample to concentrate the Cd in the samples. With this additional sample preparation step, the Cd concentration in the samples increased by factor 3 to 4 and could be thereby measured around 0.05 to 0.15 μg L^{-1}. These values were significantly above the limit of quantification of 0.006 μg L^{-1} that was calculated based on the Cd concentrations found in procedural blanks (Al-Hakkani, 2019). The Cd concentrations in the seepage water were up to two-fold higher in 2021 compared to 2022. Furthermore, Cd concentrations were highest in the N200 and lowest in the organic treatment. The average Cu and Zn concentrations in the seepage water ranged from 1.04 to 2.31 μg L^{-1} and 3.24 to 8.38 μg L^{-1}, respectively (Table S3). Similar to Cd, the seepage water concentrations of Zn and Cu differed substantially between 2021 and 2022. However, the concentrations between the different fertilization strategies did mostly not differ, except for Cu in 2022 (N100 > N200). Together, trace metal concentrations in the seepage water differed between the two years, particularly for Cd.

The annual leaching rates of Cd ranged from 0.04 to 0.30 g $(ha\ a)^{-1}$ and were up to four-fold higher in 2021 compared to 2022 (Table 1). In addition, the annual leaching rates of Cd were lowest in the organic treatment. The monthly leaching rate patterns of Cd corresponded with the monthly seepage volumes. Hence, Cd leaching peaked in May and July, but also in January during snow melting. Similarly to Cd, the annual leaching rates of Zn and Cu also differed between 2021 and 2022 and also peaked in January, May, and July 2021 (Fig. 2). However, the leaching rates of these metals were not distinguishable among the treatments. To summarize, trace metal leaching rates were higher for Cd, Zn, and Cu in 2021 compared to 2022 while the leaching rates between the treatments differed only for Cd.

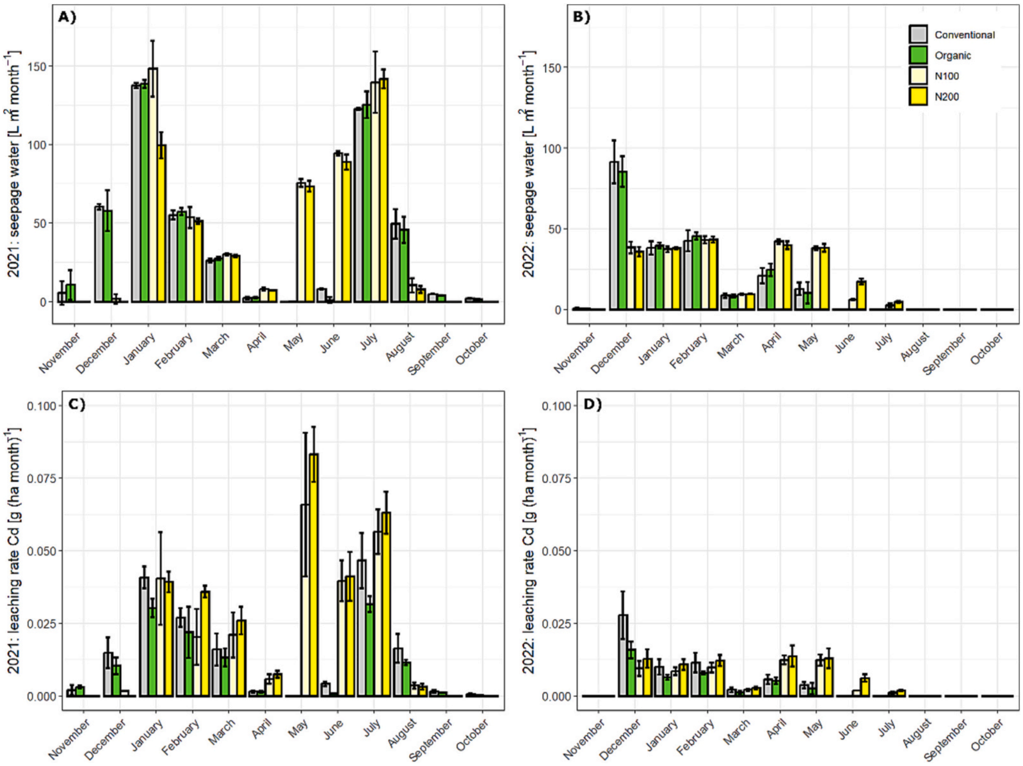

Fig. 1. Monthly seepage volume (A, B) and cadmium (Cd) leaching rates in 2021 and 2022 obtained in monolith lysimeters (C, D). The treatments 'Organic' and 'Conventional' represent organic and conventional fertilization practices according to Swiss standards. The treatments 'N100' and 'N200' represent nitrogen fertilization according to CH recommendations (N100) and twice the N fertilization rate of CH recommendations. The error bars represent the standard deviation of the mean of $n = 3$ experimental replicates.

Table 1
Annual leaching rates of trace metals in monolith lysimeters.

Treatment[a]	Crop	Year	Cd				Zn			Cu		
			g (ha a)$^{-1}$				g (ha a)$^{-1}$			g (ha a)$^{-1}$		
			mean		sd[b]		mean		sd[b]	mean		sd[b]
Conventional	Barley	2021	0.170	±	0.017	b	21.7	±	4.80	10.3	±	3.95
Organic	Barley		0.124	±	0.007	c	19.0	±	4.85	10.4	±	2.70
N100	Maize		0.254	±	0.065	a	29.2	±	11.5	11.7	±	1.89
N200	Maize		0.300	±	0.027	a	39.0	±	13.0	8.92	±	0.11
Conventional	Grass-clover ley	2022	0.061	±	0.017	ab	7.27	±	0.79	2.89	±	0.96
Organic	Grass-clover ley		0.040	±	0.006	b	7.97	±	2.15	2.96	±	0.32
N100	Maize		0.058	±	0.009	ab	8.32	±	2.19	4.35	±	0.91
N200	Maize		0.074	±	0.011	a	10.7	±	2.81	2.65	±	0.73
ANOVA 2021			$p < 0.05$				$p > 0.05$			$p > 0.05$		
ANOVA 2022			$p < 0.05$				$p > 0.05$			$p > 0.05$		

a) Treatments 'Organic' and 'Conventional' represent organic and conventional fertilization practices according to Swiss standards. The treatments 'N100' and 'N200' represent nitrogen fertilization according to CH recommendations and twice the N fertilization rate of CH recommendations, respectively. b) sd represent the standard deviation of the mean of n = 3 experimental replicates. The mean value presented is calculated by 1) the sum of all monthly leaching rates for each individual lysimeter and 2) by calculating the average of *n* = 3 experimental replicates per treatment of the annual leaching rate. Letters denote statistical differences determined by a Tukey HSD test. Letters are only given if the ANOVA was significant.

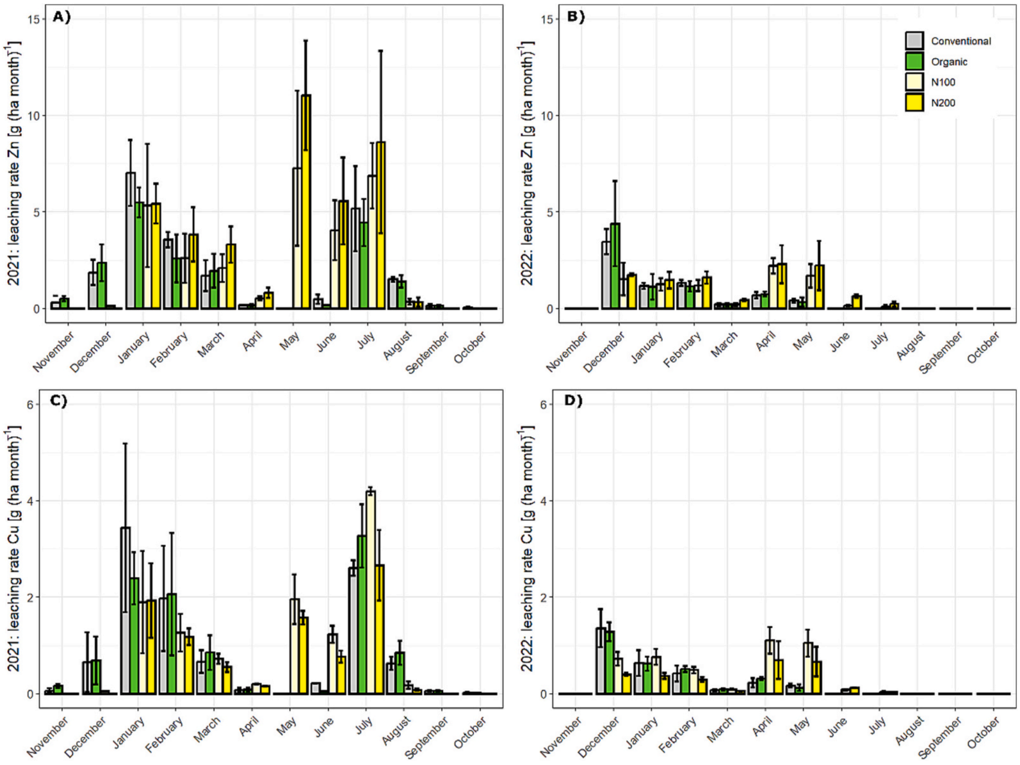

Fig. 2. Monthly leaching rates of Zn (A, B) and Cu (C, D) in 2021 and 2022 obtained in monolith lysimeters. The treatments 'Organic' and 'Conventional' represent organic and conventional fertilization practices according to Swiss standards. The treatments 'N100' and 'N200' represent nitrogen fertilization according to CH recommendations (N100) and twice the N fertilization rate of CH recommendations, respectively. The error bars represent the standard deviation of the mean of *n* = 3 experimental replicates.

3.3. Isotope source tracing in monolith lysimeters

The soluble and stable isotope labeled Cd that was added to the soil surface in autumn 2020 could be detected in the leached seepage water after one month (Fig. 3). Note, the isotope spikes were only applied to the conventional treatment. In this treatment, the ^{111}Cd: ^{110}Cd isotope ratios measured in the leached seepage water increased from natural abundance (1.024) to enriched stable isotope ratios ranging from 1.024 to 1.106. This small difference was detectable as the procedural precision allowed to detect an isotope shift of ^{111}Cd: ^{110}Cd = 0.014. The isotope enrichment in seepage water revealed that a small fraction (0.0013 ± 0.0008 %) of the total Cd that was added to the soil surface was recovered in the seepage water after one month of application. At the end of the experiment (24 months), 0.025 ± 0.0098 % of Cd was recovered in the seepage water. During the experiment, the largest increase in recovery occurred in January to March 2021 and July to September 2021. In comparison, the recovery of the Cd in the crops was 0.28 ± 0.02 % in 2021 (barley) and 0.08 ± 0.02 % in 2022 (temporary grass-clover ley). The fate of the applied Zn resembled the fate Cd (Fig. 3). However, the cumulative recovery of Zn was slightly higher than Cd in the seepage water (0.054 ± 0.0098 %) and crops (2.74 ± 0.087 %) after 24 months. The ^{65}Cu label was neither detected in the

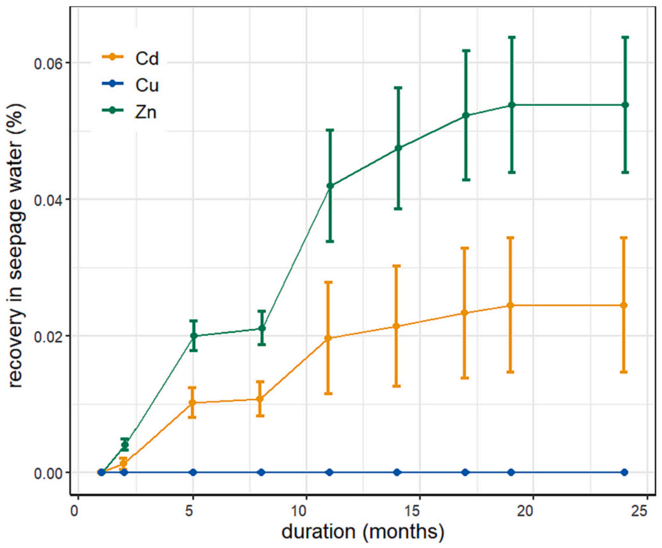

Fig. 3. Cumulative recovery of Cd, Zn, and Cu in the seepage water of monolith lysimeters. At time 0, enriched stable isotopes (^{111}Cd, ^{67}Zn, ^{65}Cu) were added to the lysimeters that were treated according to conventional fertilization practices in Switzerland. Recovery in percentage refers to the fraction of Cd, Zn, and Cu of the total quantity of enriched stable isotopes added to the lysimeter that were recovered in the seepage water. The error bars represent the standard deviation of the mean of n = 3 experimental replicates.

seepage water nor in the crops.

3.4. Trace metal mass balances in monolith lysimeters

The majority of the trace metal soil mass balances in the monolith lysimeters were positive in 2021 and 2022 (Table S4) as well as after two years (Table 2). For Cd, the inputs (fertilizers) into the lysimeters exceeded their outputs (crop harvest, seepage water) which resulted in an average soil Cd accumulation of +3.6 g ha^{-1}. Mineral fertilizer caused the highest Cd input in the conventional and in the N fertilizer treatments. The Cd inputs with organic fertilizers in the organic treatment were similar as the Cd inputs with mineral fertilizers in the conventional treatment. The Cd concentrations in the organic fertilizers were about 1000 times smaller (7 to 23 µg L^{-1}) compared to the mineral P fertilizer (9.6 mg kg^{-1}). However, the quantity of organic fertilizers applied was about 200 times larger (83′000 to 87′000 L ha^{-1}) compared the mineral P fertilizer (350 to 450 kg ha^{-1}) that were added to the lysimeters. The Zn and Cu mass balance in the monolith lysimeter differed from Cd (Table 2). Both mass balances were negative in the conventional and N100 treatment while they were positive in the organic and N200 treatment. In the conventional and N100 treatment, the Zn and Cu output with crop harvest exceeded the major inputs with fertilizers. In contrast, the Zn and Cu input with organic fertilizers clearly exceeded the output of these elements with crop harvest and seepage water.

4. Discussion

4.1. Impact of climatic conditions, crop rotation, and fertilization strategy

The annual Cd leaching rates ranged from 0.04 to 0.30 g (ha a)$^{-1}$ (Table 1). This range is similar but at the lower end when compared with leaching rates that were determined with large monolith lysimeters (0.26 to 0.90 g (ha a)$^{-1}$) and other techniques (0.04 to 1.88 g (ha a)$^{-1}$) (see Gray et al., 2021 and references therein). The mass balance calculations revealed that Cd outputs with seepage water were more than 10 times smaller than the fertilizer inputs (Table 2). In comparison to the Cd output by the harvest (0.28 to 0.61 g ha^{-1}), the output with seepage water was slightly smaller (0.16 to 0.37 g ha^{-1}). Note, the presented mass balance is lacking inputs such as soil weathering and atmospheric deposition. Imseng et al. (2019a) has recently measured these inputs in similar soils that are located in the Swiss Plateau, as the lysimeter station. According to their data, these inputs would additionally introduce about 0.25 g ha^{-1} of Cd in two years, which is similar to the seepage water output.

Table 2

Trace metal mass balances in monolith lysimeters. The mass balances comprise two crop cycles of total 24 months. The annual mass balances can be found in Table S3.

Treatment[a]	Type of input/output		Cd			Zn			Cu		
			g ha^{-1} for two crop cycles (total 24 months)								
			mean		sd[b]	mean		sd[b]	mean		sd[b]
Conventional	Mineral fertilizer	Input	3.37	±	0.40	56	±	14	7	±	0.5
	Organic fertiizer		0.44	±	0.04	233	±	20	65	±	5.2
	Crop harvest	Output	0.36	±	0.03	345	±	71	94	±	17
	Seepage		0.23	±	0.02	29	±	4.9	13	±	4.1
		Balance	**3.22**	±	**0.40**	**−85**	**±**	**75**	**−34**	**±**	**18**
Organic	Mineral fertilizer	Input	0	±	0.00	0	±	0.0	0	±	0.00
	Organic fertiizer		3.85	±	0.23	1895	±	115	503	±	29
	Crop harvest	Output	0.28	±	0.02	342	±	83	95	±	22
	Seepage		0.16	±	0.01	27	±	5.3	13	±	2.7
		Balance	**3.41**	**±**	**0.23**	**1526**	**±**	**142**	**395**	**±**	**36**
N100	Mineral fertilizer	Input	4.33	±	0.51	62	±	17	7	±	0.5
	Organic fertiizer		0	±	0.0	0	±	0.0	0	±	0.0
	Crop harvest	Output	0.57	±	0.03	752	±	40	113	±	4.5
	Seepage		0.31	±	0.07	40	±	12	16	±	2.1
		Balance	**3.45**	**±**	**0.52**	**−730**	**±**	**45**	**−122**	**±**	**5.0**
N200	Mineral fertilizer	Input	4.34	±	0.00	64	±	0.00	7	±	0.00
	Organic fertiizer		1.07	±	0.52	1181	±	102	248	±	20
	Crop harvest	Output	0.61	±	0.03	682	±	4.5	99	±	0.3
	Seepage		0.37	±	0.12	47	±	36	12	±	4.0
		Balance	4.43	±	0.54	516	±	108	144	±	20

a) Treatments ‘Organic’ and ‘Conventional’ represent organic and conventional fertilization practices according to Swiss standards. The treatments ‘N100’ and ‘N200’ represent nitrogen fertilization according to CH recommendations and twice the N fertilization rate of Swiss recommendations, respectively. b) sd represent the standard deviation of the mean of n = 3 experimental replicates for seepage water and crop harvest. For fertilizers, the standard error was calculated based on the procedural + analytical errors that were determined with replicate measurements. The sd of the final balance was calculated based on error propagation (Eq.(4)).

The Cd as well as the Cu, and Zn leaching rates were up to four times higher in the year with heavy snow and rainfalls (2021) versus the year with little rainfall and a dry summer (2022, Table 1). In addition, the water and trace metal leaching rates differed among the treatments during the year (Figs. 1–2). Particularly, the trace metal leaching rates were close to zero in the treatments with winter barley (conventional, organic) while they peaked in silage maize (N treatments) in May and June. Similarly, the evapotranspiration rates were highest in April to June for winter barley while for silage maize, the evapotranspiration peaked in June to August (Figs. S1–2). As evapotranspiration rates correspond with crop biomass and growth stage (Oberholzer et al., 2017), the distinct timing of the plant growth strongly determined the trace metal leaching rates. Similar effects may also explain the higher seepage volume and metal leaching rates in the N100 and N200 treatments compared to the other treatments in November and December 2020. Prior to our seepage water measurements, green manure grew on the N treatments while winter wheat on the conventional and organic treatments (Table S2). The green manure was already in an advanced development stage in N100 and N200 while in other treatments, the winter barley plants were still in an early stage. Therefore, our high temporal resolution data set illustrates the strong effect of distinct climatic conditions in combination with crop development.

Agricultural practices may affect Cd leaching rates as the leaching rates were higher in the conventional treatment compared to the organic fertilization treatment (Table 1). Winter barley grew on both treatments in 2021, hence, the crop development effects discussed in the previous paragraph do not explain this difference. Since 2009, the conventional treatment has received mineral fertilizers (including mineral P fertilizers) while the organic treatment has almost exclusively received organic fertilizers (mostly applied as liquid slurry). As the leaching rates between these treatments differed for Cd and not for Zn and Cu, the higher Cd leaching rates are likely related with higher Cd inputs with mineral P fertilizers (Bergen et al., 2021; Imseng et al., 2018). The mineral P fertilizer used in this study had indeed a high Cd concentration (9.6 mg kg^{-1}, or 55 mg (kg P_2O_5)$^{-1}$) as reported for other mineral P fertilizer (Smidt et al., 2011; Verbeeck et al., 2020). However, the average inputs of Cd with mineral and organic fertilizers were similar in the two treatments (Table 2). This corresponds with the non-intuitive observation of a previous study that showed that the soil accumulation of Cd can be higher in organic than in conventionally fertilized soils (Schweizer et al., 2018). In addition, the statistically non-distinguishable Cd concentrations in seepage water (Table S3) propose that the different fertilizers inputs hardly changed the capacity of the soil to bind Cd in the two treatments through e.g., increased soil organic matter content (Smolders and Mertens, 2013). Moreover, the seepage volume was not different between the organic and the conventional treatment (Fig. 1). Hence, although the Cd leaching rates between these two treatments were significantly different, they were small compared to the variation induced by distinct climatic conditions and timing of crop development. In conclusion, conventional versus organic fertilization had a minor impact on Cd leaching rates and no impact on leaching rates of Cu and Zn.

4.2. Comparison of Cd leaching rates with existing models

In the European Union (EU), soil mass balance models are used to assess the risk for Cd in fertilizers (Bergen et al., 2021). These models integrate Cd stocks (i.e. Cd concentrations in soils), inputs (atmospheric deposition, fertilizer inputs), and outputs (crop offtake and leaching). For the Cd leaching rates, several models exist that predict seepage water concentrations based on the Cd distribution coefficients (i.e. soil extract to determine liquid vs. solid phase partitioning, Shaheen et al., 2013), soil pH, soil organic carbon content, total soil Cd concentrations, and in some cases the clay content (see Bergen et al., 2023 and references therein). These parameters have been typically determined in topsoils. The predicted Cd concentration in the seepage water is then multiplied with a precipitation excess (i.e. seepage volume) of 200 L m^{-2} for non-Mediterranean regions. Such models have provided the scientific basis for policy makers to set the EU limit for Cd in mineral fertilizers to 60 mg kg^{-1} Cd per kg P_2O_5 (Bergen et al., 2021; EU, 2019).

For comparison with the Cd concentrations and leaching rates measured in this study, we applied the five different models referenced in Bergen et al. (2021). To this end, we used the soil parameters that were quantified at the time of installation of the lysimeter facility in 2009 (Table S1). The total soil Cd concentration that was determined in this study for a mixed sample of the entire profile (see 2.2). In addition, we defined ranges for each soil parameter to account for soil heterogeneities, analytical uncertainties, and potential soil chemical changes since 2009 (Table S5). The models were applied for the A horizon (0-25 cm, Table 3) and a weighted mean of the entire soil profile (Table S 6). The models were further applied based on 1000 random latin hypercube samples of parameter combinations drawn within these defined ranges to quantify median Cd concentrations in leaching water. Boxplots that show uncertainty ranges for modelled Cd leaching rates are shown in Fig. S3a-c.

The median Cd concentrations in the seepage water ranged from 1.2 to 5.1 μg L^{-1} based on the different models applied (Table 3). These modelled concentrations were factor 31 to 134 times higher than the seepage water concentrations measured in this study. According to Bergen et al. (2023), the large variation in the outcome of the different models can have several reasons. For instance, the difference between model 1 and 2 is that soils with high Cd concentrations were excluded to parameterize the model. Other models included data that were obtained with old analytical techniques (AAS) or techniques with high Cd detection limits (ICP-OES) as well as Cd concentration data that was obtained in pore water and/or diluted salt extracts. These different laboratory protocols may have induced distinct results for Cd distribution coefficients and thereby contributed to the distinct model parameterizations. The modelled Cd leaching rates were 17 to 76 times higher than the measured leaching rates in this study (Table 3). These factors were smaller compared to the Cd seepage water concentration because for all modelled Cd leaching rates, a seepage volume of 200 L m^{-2} was used as suggested in Six and Smolders (2014). By using a seepage volume of 500 L m^{-2} (i.e. similar to year 2021 with heavy rainfalls), the modelled Cd leaching rates were 44 to 189 times higher than the ones measured in this study. An integration of these most extreme factors (44 and 189) into the soil mass balances of the conventional treatment (Table 2) would lead to a net depletion of Cd in the soil ranging from −6 to −40 g (ha)$^{-1}$ for the two growing seasons studied. These scenarios propose that a fertilizer below the defined threshold of 60 mg Cd (kg P_2O_5)$^{-1}$ as used in this study (55 mg Cd (kg P_2O_5)$^{-1}$) mostly poses no risk since the net Cd accumulation in the soil is negative. However, the outcome of the data measured in this study would propose that the fertilizer used poses a risk as the accumulation rate of Cd was >3 g (ha a)$^{-1}$ (Table 3). Hence, using the same fertilizer and applications for a decade would result in +60 g (ha a)$^{-1}$, which corresponds to about a 0.5 % of the total Cd stock and about 16 % of the DTPA extractable Cd pool in the soil (Table S1). Hence, our study would suggest to set the threshold to lower than 60 mg (kg P_2O_5)$^{-1}$ as it has been discussed in the EU parliaments (Marini et al., 2020). This simple scenario illustrates the importance of adequate models to predict Cd leaching rates and soil mass balances for risk assessments.

Our data (Table 3) and previously obtained data (Gray et al., 2021) suggests that the modelled Cd seepage water concentrations are overestimated. However, experimental determinations of leaching rates are not free of artifacts, including monolith lysimeters (Weihermüller et al., 2007). The large monolith lysimeters used in this study have several advantages compared to other techniques, most important might be the fact that they provide undisturbed soil cores and average out small scale heterogeneities through their size (Meissner et al., 2014). Previously, it was hypothesized that Cd leaching rates obtained with suction cups (Imseng et al., 2018) may underestimate the rates as the suction cups

Table 3

Comparison of Cd concentrations in seepage water and Cd leaching rates with modelled and measured data of this study (see Fig. S3 for the full ranges of the model estimates and Table S6 for all soil horizons).

	Cd concentration in seepage water [μg L^{-1}]					*leaching rate [g ha^{-1} a^{-1}]*				
Model used[a]	1	2	3	4	5	1	2	3	4	5
Estimated[b]	5.1	3.2	2.0	1.2	2.7	10	6.4	4.0	2.3	5.3
Measured	0.019–0.069					0.04–0.30				
Average difference[a,b,c]	134	85	52	31	70	76	48	29	17	39

[a] Models source from de Vries et al. (2011) [3], Römkens et al. (2018) [4], Römkens and Smolders (2018) [5], Six and Smolders (2014) [1, 2]. See more details in Bergen et al., 2023.

[b] Estimated (A-horizon 0-25 cm) for the median concentrations and leaching rates based on the models mentioned in a). More information on the median calculation and model sensitivities regarding their input data can be found in Fig. S3 and Tables S5–6. The Cd leaching rates were calculated with 200 m L^{-2} a^{-1} seepage volume as proposed by Six and Smolders, 2014. As input for total Cd in the soil, the total concentration of a mixed soil sample (i.e. including all soil horizons) was taken. This Cd concentration was determined multiplying the total concentration in the soil determined with hydrofluoric acid (see chapter 2.2) with the factor 0.73 to obtain an aqua regia extractable Cd concentration (Bergen et al., 2021).

[c] This is a factor built by taking the ratio of modelled: measured Cd concentrations or leaching rates. 76 means the model predicted the corresponding value 76 times higher than the measured value here 1.35 m depth.

may filter Cd absorbed to soil colloids (McLaughlin et al., 2020). As the annual leaching rates of the present study were similar to the suction cup study of Imseng et al. (2018), this critique could be also applied to this study. During sampling campaigns of this study, we noticed soil particles in the sampled seepage water, particularly after heavy rainfalls and/or snow melting. As we homogenized and acidified the sampled seepage water (see Section 2.2), we expect that the Cd that was sorbed to colloids was recovered. Hence, at least part of colloidal Cd was sampled in this study. Moreover, a recent study revealed that colloidal Cd in seepage water accounted for about 30 % (Bergen et al., 2023). Taken together, colloidal Cd may have induced a minor underestimation of the Cd leaching rates, however, it cannot fully explain the discrepancy between the measured and the modelled data presented in Table 3.

The lysimeters used in this study were free draining lysimeters that are not in contact with the groundwater table, but exposed to atmospheric pressure (Prasuhn, 2016; Weihermüller et al., 2007). In the lysimeters used here, this could induce water logging at the interface of the lowest horizon and the quartz sand layer. The water logging could temporarily drop the soil redox potential, thereby reductively dissolve iron (Fe) and manganese (Mn) oxides (Kirk, 2004). These transformations can increase soil pH and thereby also increase the sorption of trace metals to the soil solid phase (Weber et al., 2009; Wiggenhauser et al., 2021). This change in soil chemistry could lead to an underestimation of the trace metal leaching rates in the lysimeter compared to 'real' soils in the field. However, the soil organic carbon that facilitates the reductive dissolution of Fe and Mn (Dong et al., 2023; Kirk, 2004) was very low in the lowest horizons (Table S1). In addition, the sand layer with gradually increasing grain sizes underneath the soil profile was established to minimize this water logging effect (see chapter 2.1).

Finally, the models were fitted based on soil extracts from the topsoil while we measured the Cd seepage water concentration in a depth of 1.35 m. Table S6a shows that the Cd concentrations of the model outputs can vary up to factor 20 among the different soil horizons and up to factor 10 compared to the weighed mean concentrations of the entire profile (Table S6a-b). In addition, the modelled concentrations were lowest in the A-horizon due to the higher soil pH and organic carbon content compared to the other horizons. Nevertheless, even if the direct comparison of the lysimeter data obtained here with the modelled data is limited, our data and previously obtained experimental data that used different techniques to determine Cd leaching rates at different soil depths (Cambier et al., 2014; Gray et al., 2021; Imseng et al., 2018) suggest that the current models used to predict Cd leaching rates need to be refined.

4.3. *Direct transfer of trace metals into seepage water is small*

A pot study that applied isotope source tracing revealed that >97 % of the Cd that was applied with a mineral P fertilizer remained in the soil (Bracher et al., 2021). There, up to 75 % of the Cd was deposited in the mobile soil fractions. It was suggested that the fertilizer applied Cd could be taken up with the next crop or leached into the groundwater. Our study showed that a minor fractions of the soluble Cd spike that mimicked mineral P fertilizer were transferred to the following crop (< 0.1 %). In addition, the direct transfer of fertilizer applied Cd into the seepage water was small (< 0.03 %, Fig. 3). These results suggested that most of the fertilizer applied Cd remained in the soil where Cd was mixed with the Cd that that had been already present in the soil.

A major input pathway of Cu and Zn into agricultural soils is pig manure as these elements are used as growth promoter for small piglets (Brugger and Windisch, 2015). Hence, excessive inputs of Cu and Zn with pig manure can lead to a severe soil accumulation of these elements (Imseng et al., 2019b; Ostermann et al., 2015) and potentially also an increased input of these elements into the groundwater (Ogiyama et al., 2005). In this study, organic fertilizers were the major Cu and Zn input and induced an accumulation of Cu and Zn in soils, particularly in the organic treatment (Table 2). The Cu and Zn concentration was unlike in pig slurry not elevated in these fertilizers (Cu < 4 mg kg^{-1}; Zn < 13 mg kg^{-1}) compared to the soils (Cu: 1.88 to 6.15 mg kg^{-1}, Zn: 9.67 to 20.7 mg kg^{-1}). Hence, high inputs of organic fertilizers with non-elevated Cu and Zn concentration can lead to a soil accumulation of these trace metals. These findings are in agreement with Gross et al. (2021) who showed a significant correlation with the number of livestock per ha and Cu and Zn inputs into the soil. Hence, Cu and Zn soil mass balances should not only be established for pig slurries that are concentrated in Cu and Zn, but also for organic fertilizers with background concentrations of trace metals.

Generally, the output of Cu and Zn with seepage water was >5 to 10 times lower than the major in- and outputs of the monolith lysimeters (Table 2). Moreover, the soluble Zn spike that was applied to the soils was small but detectable in the seepage water (Fig. 3). However, Cu was not detectable at all. Therefore, the mobility of Cu in the soil profile was smaller than for Zn (and Cd). This observation corresponds with partitioning coefficients of these metals in soils that indicate that Cu binds stronger to soils than the other two metals and a previous study that applied enriched ^{65}Cu spiked pig manure to an alkaline soil (Ostermann et al., 2015). Such a labeling of the pig manure is more realistic than the application of a soluble spike as done in our study since the chemical speciation of the Cu in the fertilizer may strongly impact its mobility in the soil profile (Yamamoto et al., 2018). The ^{65}Cu from the pig manure could be only detected in the top 5 cm of the soil after 53 days of fertilizer applications (Ostermann et al., 2015). This previous study that applied a labeled pig manure to an alkaline soil and our study that applied a soluble 'fertilizer' to a weakly acidic soil strongly suggest that fertilizer applied Cu is mostly retained in soils and that the direct transfer of Cu and Zn to the seepage water is very small.

5. Conclusion & Implications

In this study, large monolithic lysimeters were used to determine precise trace metal leaching rates for two years. It revealed the output of trace metals from the soil profile with seepage water is small compared to the trace metal inputs with fertilizers. A comparison of our results with models that predict Cd leaching rates suggest that these models overestimate Cd leaching rates and thereby underestimate the risk of Cd accumulation in soils. Hence, more studies in state-of-the-art lysimeter facilities and/or undisturbed large soil columns would help to refine models that predict trace metal leaching and soil accumulation on a large scale. Such a refinement of soil mass balances remains relevant for Cd as Cd in crops remains a major source of Cd intake by humans (Zhao et al., 2022). In addition, precise leaching rates and soil mass balances for Cu and Zn may also gain importance with the attempts from the EU towards a circular economy that will introduce different fertilizer materials to the soils (Bünemann et al., 2024; Chojnacka et al., 2020; Mayer et al., 2019). Our and previous studies illustrated that not only fertilizer materials that are known to be enriched in trace metals such as mineral P fertilizer and pig manure, but also high application rates of organic fertilizers can contribute to a trace metal accumulation in soils (Gross et al., 2021; Schweizer et al., 2018). This is particularly the case in intensive farming systems irrespective if they are following conventional or organic farming standards. Finally, our temporally resolved data illustrated how Cd, Cu, and Zn leaching rates can strongly vary with a combination of distinct climatic conditions (i.e. heavy rainfall, vs. dry periods) and crop development. Given that climate change is expected to increase the frequency of such extreme weather periods in Europe (IPCC, 2021), current leaching and soil mass balance models for trace metals should integrate these meteorological variations and crop rotations.

Funding sources

No specific funding sources to declare.

CRediT authorship contribution statement

Matthias Wiggenhauser: Writing – review & editing, Writing – original draft, Visualization, Validation, Supervision, Project administration, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **David Illmer:** Writing – review & editing, Investigation, Formal analysis, Data curation. **Ernst Spiess:** Writing – review & editing, Data curation. **Annelie Holzkämper:** Writing – review & editing, Visualization, Validation, Data curation. **Volker Prasuhn:** Writing – review & editing, Resources, Methodology, Conceptualization. **Frank Liebisch:** Writing – review & editing, Resources, Methodology, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgements

We thank Clay Humphrys (Agroscope), Karin Meier Zimmermann (Agroscope), Geremia Pellegrini (ETH Zurich), and Laurie Schoenholzer (ETH Zurich) for the support at the Lysimeter facilities and the samplings as well as Benoit Bergen and Erik Smolders from KU Leuven for the provision of the spreadsheet to model the seepage water concentrations and the members of the COST Action CA19116 PLANTMETALS (COST, European Cooperation in Science and Technology, www.cost.eu) for knowledge exchange. Graphical abstract was created with Biorender.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2024.171482.

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