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Impact of organic and conventional farming systems on wheat grain uptake and soil bioavailability of zinc and cadmium

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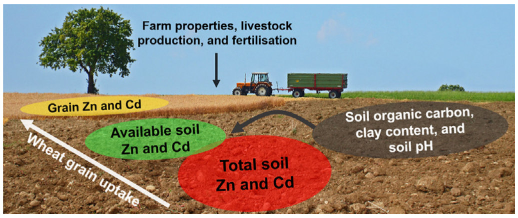
HIGHLIGHTS

- Soil Zn and Cd were promoted by soil organic matter due to higher input and binding.
- Organic farming with compost had more available soil Cd than conventional farming.
- Grain Zn was decoupled from soil Zn.
- Livestock production increased soil and grain Cd indicating contamination.
- In the field, a combination of management and soil properties influenced Zn and Cd.

GRAPHICAL ABSTRACT



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ABSTRACT

Zinc (Zn) deficiency is a widespread problem in human nutrition and wheat grains are a major source of Zn intake in large parts of the population. It remains unclear to what extent organic and conventional farming practices, differing in organic matter management, influence Zn availability and uptake by wheat grains. Factors leading to an increased Zn uptake may also increase the Cd uptake in wheat grains, which can be harmful for humans. Here, we investigated the effects of different farming practices on Zn and Cd concentrations in wheat grains and their relationships with total and available soil Zn and Cd concentrations, and other soil properties. In northern Switzerland, 28 farms were sampled including 11 organic farms with compost use, 10 organic farms without compost use, and 7 conventional farms without compost use. Soil organic matter was a key factor for soil Zn and especially Cd concentrations across all three farming systems. Total and available soil Cd concentrations as well as soil organic carbon concentration (SOC) were significantly higher on the organic farms with compost use than on the conventional farms. However, only the compost farms with livestock showed significantly higher grain Cd concentrations in comparison to conventional and organic farms without compost use, although a nested effect of cultivar within the system also had an influence. In contrast to Cd, the soil and grain Zn concentrations showed no significant farming system effect although there was a correlation between total soil Zn and SOC when all farms were pooled. Grain Zn was decoupled from soil Zn indicating that under agricultural field conditions the farming systems are a minor factor in increasing grain Zn. Our study suggests that the Zn and Cd soil and grain concentrations were mediated by a combination of on-farm organic matter management, soil properties, cultivar, and livestock production.

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1. Introduction

Increasing zinc (Zn) in edible plant parts is a strategic aim in agricultural systems to combat widespread Zn deficiency in human nutrition (Cakmak, 2008; Cakmak and Kutman, 2017; White and Broadley, 2011). The HarvestPlus program has set a target concentration of 38 mg kg^{-1} Zn in wheat grains (Bouis and Welch, 2010). In agricultural soils, the availability of soil Zn for uptake by crop plants is limited by its solubility, which is governed primarily by adsorption to mineral surfaces, complexation with organic matter and formation of precipitates (Baird and Cann, 2005; Smolders and Mertens, 2013). Due to its chemical similarity with Zn, the availability of soil cadmium (Cd) is affected in a similar manner by the same soil factors (Hart et al., 2002). However, Cd threatens human health and the environment and, thus, interactions between Zn and Cd availability and uptake should be carefully monitored. In particular, the availability of Zn and Cd in the soil is dependent on soil organic matter (SOM), oxides, clay particles, and pH (Schulin et al., 2009; Smolders and Mertens, 2013). The affinity of Zn and Cd for sorption on soil particles can be >10 times higher on organic matter than on mineral particles (Lair et al., 2007b). As agricultural practises can have a major impact on SOM and soil pH (Bolan et al., 2001; Six et al., 2000), it is important to understand how they influence available Zn and Cd concentrations in agricultural soils. For food safety reasons it is especially important to relate soil Zn and Cd to their uptake by wheat grains to determine how availability translates into the edible parts of crop plants. Previous studies showed that for some cultivars the Zn and Cd accumulation in grains might be more strongly affected by soil properties than others (Gao et al., 2011) whereas the different soil properties of sites had a higher impact than crop cultivars (Oliver et al., 1995; Wångstrand et al., 2007).

Various studies investigated how organic compounds affect Zn and Cd uptake by crop plants. In a hydroponic experiment, the addition of citrate and histidine increased Zn uptake of wheat due to soluble complex formation of Zn with these organic acids, comparing nutrient solutions with the same free Zn concentration (Gramlich et al., 2013). Soil microorganisms can increase soil Zn availability by exuding organic ligands (Altomare and Tringovska, 2011). Mycorrhizal plants were observed to have more Zn available, while Cd toxicity was reduced due to a potential discrimination of the arbuscular mycorrhiza between Zn and Cd (Janoušková et al., 2006). These greenhouse and pot experiments provided important insights, however, the impact of SOM management on Zn and Cd availability remains elusive in real farm environments.

In addition to the complexation by organic ligands and sorption at organic matter surfaces, Zn and Cd can also be sorbed and complexed at mineral surfaces like clay minerals or (hydr-)oxides (Fonseca et al., 2011; Sipos et al., 2008). Organo-mineral associations were shown to provide important interfaces for the binding of heavy metals and can be prominent factors for the binding and mobilisation of soil Zn and Cd (Arias et al., 2005; Leinweber et al., 1995).

The addition of fertilisers or amendments containing organic matter can enrich soils with heavy metals due to metal contents of the applied materials exceeding natural inputs (Facchinelli et al., 2001). Animal feed is supplemented with Zn to improve animal health and livestock productivity and the majority of the supplemented Zn is not retained by the animals and excreted (Bolan et al., 2004; Gubler et al., 2015; Schultheiß et al., 2004). The heavy metal concentrations in manure vary depending on the farming system and the feed and supplements used (Keller et al., 2002; Menzi and Kessler, 1998; Menzi et al., 1999; Möller and Schultheiß, 2015). In German dairy production, on-farm grown fodder introduced 39% of the added Zn and 71% of the Cd into cow sheds, whereas protein-rich external feed accounted for a similar range of Zn and much less Cd (Schultheiß et al., 2004). In addition, the recycling of plant residues and land management was found to influence metal dynamics and plant uptake (Düring et al., 2003; Mench, 1998; Oliver et al., 1993). While many studies have looked at the on-farm flows of heavy metals in livestock production, only a few studies have investigated to what extent heavy metals are retained and mobilised in agricultural soils (Helfenstein et al., 2016).

In this study, we investigated how agricultural cropping and livestock production systems influence Zn and Cd concentrations in wheat grains and how these effects relate to soil Zn and Cd availability and other soil factors. We sampled soils and wheat grains on farms in northern Switzerland categorised in three differing farming systems, with and without livestock production: organic farms with compost use, organic farms without compost use, and conventional farms without compost use. The objectives of the study were (i) to relate total and available soil Zn and Cd concentrations to wheat grain Zn and Cd concentrations and (ii) to assess the role of management practices and soil properties in these relationships.

2. Methods

2.1. Study site and farm characteristics

The 28 farms included in this survey were located at elevations between 340 and 954 m above sea level around Zurich in northern Switzerland (Fig. 1). The sampled soils were Cambisols (WRB) with an average clay-sized particle content of 25 ± 1.2% and a range of 16–41%. The sampled soils did not significantly differ in texture, cation exchange capacity (CEC), pH, and bulk density between the three farming systems we distinguished in this study. The climate is temperate and humid. The annual mean temperature at the centrally located city Zurich is 8.5 °C and the average annual precipitation 1136 mm. The 28 farms were classified as organic farms with compost use (COMP; $n = 11$ with 6 livestock farms), organic farms with use of uncomposted manure (ORG; $n = 10$ with 8 livestock farms) and conventional farms with integrated fertilisation of synthetic fertilisers and minor amounts of uncomposted manure (CON; $n = 7$ with 6 livestock farms).

We assessed the management practices used on the whole farms as well as those applied specifically on the sampled fields, where farmers grew winter wheat (*Triticum aestivum* L.) or spelt (*Triticum aestivum* subsp. *spelta* L.), in 2015. In particular, the winter wheat cultivars Camedo, Fiorina, Ludwig, Forel, and Siala were grown on the organic farms with compost use. On the organic farms without compost use, farmers grew Wiwa, Bockris, Titlis, Claro Bio, and Oberkulmer Rotkorn, whereas one farmer grew spelt. The conventional farmers grew the cultivars Aszita, Scaro, Arina, Zürcher Oberländer Rotkorn, Wiwa, Tengri, Titlis, Runal, Fiorina, and Claro Bio. By means of questionnaires, the following data were recorded: plot and farm size, livestock production, and fertilisation. The organic C (C_{org}), total N (N_{tot}), and mineral N (N_{min}) inputs during the whole crop rotation as well as during wheat cultivation were estimated based on fertiliser input and using standard values for nutrient contents of the various fertilisers according to Flisch et al. (2009) and Schleiss (2015; Table A.1). The N input from inorganic fertilisers was calculated from data provided by the fertiliser suppliers, whereas the total N content was assumed to equal the mineral N contents (Table A.2). The individual data of the farms is given in Table A.3.

2.2. Sampling and analysis

We collected soil and grain samples approximately 3 days prior to harvest from fields cultivated with wheat in 2015. One field was sampled per farm. Soil cores were extracted 4 times at 0–20 cm depth within 10 m distance to a representative location and merged to one composite sample per farm. The soil samples were dried for 48 h at 40 °C until constant weight, sieved <2 mm, and ground. The bulk density of 100 cm^3 soil cores was analysed in triplicates at 2.5–7.5 cm and 12.5–17.5 cm respectively and averaged across the replicates and both depths.

We analysed the clay content by treating 10 g of each sample with an excess of H_2O_2 (30%) until no further oxidation was observed. The

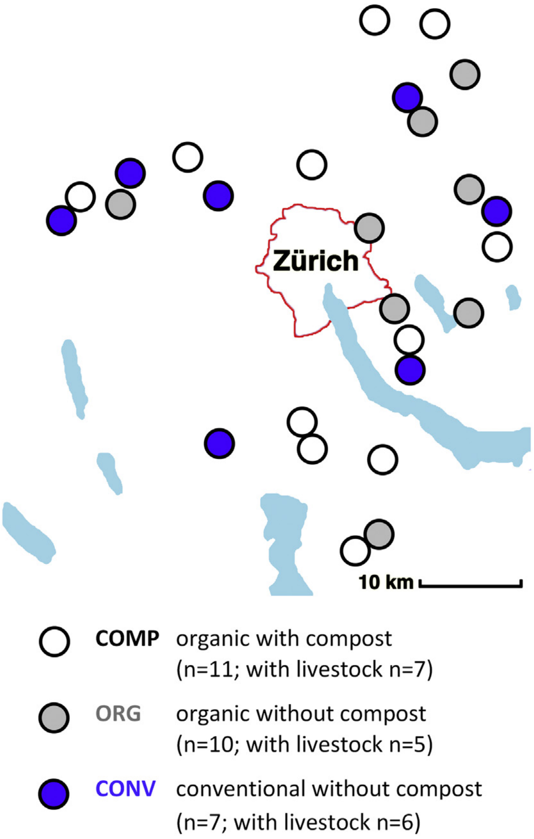

Fig. 1. Location of study sites in the area of Zurich.

oxidised samples were boiled after adding an additional 500 ml H_2O for 1 h to remove excess H_2O_2. Then, the samples were dispersed with sodium hexametaphosphate (10%) from which suspensions were pipetted to measure the amount of clay and silt (Gee and Bauder, 1986).

The CEC was measured by adding an exchange solution made from 0.1 M $BaCl_2$ and 0.03 M triethanolamine buffer adjusted to pH 8.1. After 12 h the samples were shaken and the cations in the filtrate were measured: H^+ by titration with 0.05 M HCl and Na^+ und K^+, Mg^{2+}, Ca^{2+} by atomic absorption spectroscopy. The cation exchange capacity was calculated from the sum of these cations.

We analysed total N in the samples with dry combustion using an NCS analyser FlasEA 1112 Series (Thermo Fisher Scientific, Waltham, USA). To determine the soil organic carbon (SOC) concentration, both the total and inorganic carbon were analysed by catalytically aided combustion oxidation with a total organic carbon analyser using a TOC Analyser (TOC-L, Shimadzu, Kyoto Japan).

The total metal concentrations were extracted by aqua regia wet digestion. Briefly, we mixed 1 g ground soil with 2 ml deionised water, 2 ml HNO_3 (70%), and 6 ml HCl (37%). Thereafter, the suspension was extracted for 90 min at 120 °C in a DigiPREP digestion system (SCP Science, Baie-d'Urfé, Canada) and filtered >8 μm. To extract available metal concentrations, the soil samples were shaken for 2 h on a horizontal shaker with diethylenetriaminepentaacetic acid (DTPA) according to Lindsay and Norvell (1978). After extracting total and available metal from the soils, we measured the solutions with a 5100 ICP-OES (Agilent Technologies, Santa Clara, USA). We included the International Soil-Analytical Exchange reference standards 900 and 921 (http://www.wepal.nl/) in the analysis indicating 105% recovery.

On each field, we sampled the grains from four areas of 1 m^2, located within the area from which the soil samples were taken, by manual harvest and combined them to one composite sample per farm. The grain samples were threshed, dried for 48 h at 60 °C until constant weight, and ground. The yields were calculated with a grain moisture of 15% according to the moisture analysis by near-infrared spectroscopy (Infratec 1241 Grain Analyser, Gerber Instruments, Switzerland).

To extract Zn and Cd from the grains, we mixed 100 mg of ground grain samples with 1 ml HNO_3 (65%) and 2 ml H_2O_2 and digested in a Microwave turboWave (MLS GmbH, Leutkirch, Germany). The grain Zn concentrations were measured with the ICP-OES as previously described whereas the grain Cd concentrations were determined with a 7500ce ICP-MS (Agilent Technologies, Santa Clara, USA). The International Plant-Analytical Exchange references 200 and 783 (maize shoots and wheat grains; http://www.wepal.nl/) were included in the analysis indicating 97% recovery.

2.3. Statistical analysis

The data was statistically analysed with SAS 9 (SAS Institute Inc., USA). We assessed the assumptions for variance analysis such as normal distribution and homogeneity of variances through QQ and residual plots. Analysis of variance (ANOVA) was carried out using linear models where the farming system was included as a main effect. When analysing grain properties, the wheat cultivars were included and tested as a nested effect within system. If the ANOVAs were significant ($p < 0.05$ significant, $p < 0.1$ tendency), we compared the treatments pairwise according to Tukey's HSD test and analysed for interactions in the case of multiple variables.

3. Results

3.1. Farm system properties

The conventional farms showed a more intense livestock production on average, as indicated by a tendency towards higher livestock density and concentrate feed density (Table 1). The organic C input on the organic farms with compost use averaged 4.8 times that of conventional farms during the analysed wheat year (Table 1). Over the whole crop rotation, the average input of organic C increased in the order CON < ORG < COMP but there was no significant difference between the farming systems (Table 1).

The total amounts of applied N during the wheat year increased in the order ORG < CON < COMP. In contrast to total N, the mineral N input on the conventional farms was 2.8 times that of both the organic farming systems (Table 1). Over the whole crop rotation, the mineral N input in conventional farms was 3.6 times that of organic farms with compost use and 1.7 times that of organic farms without compost use (Table 1).

The organic farms with compost use had a tendency towards higher SOC concentration and SOC:N ratios than the conventional farms, while the organic farms without compost use were in between (Table 1). The soil pH and the bulk density did not show significant differences between the farming systems (Table 1). The wheat grain yield of conventional farms averaged 1.3 times the yield of organic farms with and without compost use (Table 1) but grain N was not significantly different. When comparing only farms with livestock, we found a similar pattern for the soil characteristics except for the bulk density, which was significantly higher on conventional farms (1.3 g cm^{-3}) than on organic farms with and without compost use (1.2 g cm^{-3}; ANOVA $p = 0.03$). The spatial distribution of the farms with livestock was similar to those without.

3.2. Metal concentrations in soil and grain

The organic farms with compost use showed the highest mean total and DTPA-extractable soil Cd concentrations (Table 2). Their total soil Cd concentration was 1.7 times that of conventional farms (Table 2) and their DTPA-extractable soil Cd concentration was also significantly higher than the conventional farms. The grain Cd did not show significant differences between the farming systems whereas when cultivar

Table 1
Farm characteristics and livestock production properties (mean ± standard error). Three farming systems were investigated including 11 organic farms with compost use (COMP), 10 organic farms without compost use (ORG), and 7 conventional farms without compost use (CON). Values with the same letter within one row are not significantly different ($p < 0.05$). Letters in brackets indicate a tendency ($p \leq 0.1$).

	COMP	ORG	CON	ANOVA
Farm properties				
Total farm size [ha]	31.5 ± 4.8	34.5 ± 7.2	38 ± 7.3	$p = 0.79$
Cropland [ha]	10.9 ± 2.3	10.7 ± 3.2	17.3 ± 5.4	$p = 0.39$
Livestock production				
Livestock density [LMU ha^{-1}]	0.8 ± 0.2 (a)	0.8 ± 0.2 (a, b)	1.4 ± 0.3 (b)	**($p = 0.07$)**
Basic feed [t $(ha\ yr)^{-1}$]	6 ± 1.1	3.2 ± 1.1	9.1 ± 4.9	$p = 0.41$
Concentrate feed [t $(ha\ yr)^{-1}$]	0.6 ± 0.3 (a, b)	0.1 ± 0.1 (a)	1.1 ± 0.4 (b)	**($p = 0.09$)**
Mineral feed supplements [kg $(ha\ yr)^{-1}$]	22 ± 7	14 ± 3	28 ± 16	$p = 0.68$
Fertilisation during wheat year				
C_{org} [kg $(ha\ yr)^{-1}$]	3575 ± 793 a	900 ± 281 b	738 ± 277 b	**$p = 0.003$**
N_{tot} [kg $(ha\ yr)^{-1}$]	265 ± 40 a	115 ± 30 b	211 ± 26 a, b	**$p = 0.02$**
N_{min} [kg $(ha\ yr)^{-1}$]	54 ± 11 a	61 ± 15 a	162 ± 7 b	**$p < 0.0001$**
Fertilisation during crop rotation				
C_{org} [kg $(ha\ yr)^{-1}$]	2973 ± 534	2432 ± 519	2146 ± 526	$p = 0.54$
N_{tot} [kg $(ha\ yr)^{-1}$]	208 ± 31	210.9 ± 37	255 ± 38	$p = 0.60$
N_{min} [kg $(ha\ yr)^{-1}$]	40 ± 10 a	87 ± 15 b	145 ± 10 c	**$p < 0.0001$**
Soil properties				
Clay <2 μm [%]	24.4 ± 2.2	25.9 ± 1.3	24.5 ± 3.3	$p = 0.86$
CEC [cmol + kg^{-1}]	21.4 ± 2.1	23.5 ± 2	18.7 ± 2.2	$p = 0.36$
pH ($CaCl_2$)	6.5 ± 0.1	6.6 ± 0.2	6.5 ± 0.1	$p = 0.95$
SOC [g kg^{-1}]	26.5 ± 3.1 (a)	23.8 ± 2.9 (a, b)	17.4 ± 1.3 (b)	**($p = 0.1$)**
SOC:N	8.8 ± 0.2 (a)	8.3 ± 0.2 (a, b)	8.1 ± 0.2 (b)	**($p = 0.1$)**
Bulk density [g cm^{-3}]	1.2 ± 0.06	1.2 ± 0.05	1.3 ± 0.02	$p = 0.38$
Grain properties				
Yield [t ha^{-1}]	5.1 ± 0.4 a	5 ± 0.4 a	6.7 ± 0.7 b	**$p = 0.05$**
Grain N [g kg^{-1}]	18.6 ± 0.3	17.7 ± 1	18.9 ± 1	$p = 0.52$

P-values are displayed in bold when $p < 0.05$ and in bold and brackets when $p \leq 0.1$.

was included as a nested effect within the system effect, a better fit was achieved (Table 2). If the farming systems were compared only among farms with livestock, the grain Cd concentration of organic farms with compost use averaged 1.4 times that of organic farms without compost use and conventional farms (Fig. 2). In addition, comparing farms with and without livestock independent of the farming system, the grain Cd concentration and the ratio of grain Cd to grain N concentrations was higher in farms with livestock, especially when including the nested effect of cultivar within the livestock effect (Fig. 3e, f), but total soil Cd was not, nor was SOC (Fig. 3c, d).

The soil and grain Zn concentrations did not significantly differ among farming systems (Table 2). The soil and grain Zn concentrations on organic farms with and without compost use were on average 17% higher than the one on the conventional farms, although this was not significant. The ratio of grain Zn to grain N concentrations (including a nested effect of cultivar within system) was higher on organic farms without compost use and tended to be higher on the organic farms with compost use compared to the conventional farms (Table 2). Farms with livestock showed a tendency towards higher soil Zn than farms without livestock (Fig. 3a), but grain Zn did not show significant differences (Fig. 3b).

3.3. Key factors for soil Zn and Cd concentrations and wheat grain uptake

We found that higher SOC concentration and CEC correlated positively with total soil Zn and Cd concentrations as well as with DTPA-

Table 2
Metal concentration in soil and wheat grains from various farming systems (mean ± standard error). Three farming systems were investigated including 11 organic farms with compost use (COMP), 10 organic farms without compost use (ORG), and 7 conventional farms without compost use (CON). Values with the same letter within one row are not significantly different ($p < 0.05$). Letters in brackets indicate a tendency ($p \leq 0.1$). For grain properties, the nested effect of cultivar within system is given in the footnotes when significant ($p < 0.05$).

	COMP	ORG	CON	ANOVA
Zn				
Total soil Zn [mg kg^{-1}]	65.3 ± 4.4	64.8 ± 4.3	62.6 ± 3.4	$p = 0.92$
Available soil Zn [mg kg^{-1}]	2.1 ± 0.3	2.1 ± 0.4	1.6 ± 0.4	$p = 0.65$
Available: total soil Zn [%]	3.4 ± 0.6	3.2 ± 0.6	2.6 ± 0.6	$p = 0.74$
Grain Zn [mg kg^{-1}]	33.2 ± 1.9	34.1 ± 2.7	28.9 ± 1.3	$p = 0.27$
Grain Zn: grain N [%]	0.18 ± 0.01 a (b)	0.19 ± 0.01 a	0.15 ± 0.01 b	**$p = 0.02^{\dagger}$**
Cd				
Total soil Cd [mg kg^{-1}]	0.38 ± 0.05 a	0.33 ± 0.03 a, b	0.22 ± 0.03 b	**$p = 0.05$**
Total soil Cd: CEC [μg $cmol+^{-1}$]	17.5 ± 1.1 a	14.3 ± 1.1 a, b	12 ± 1.5 b	**$p = 0.01$**
Available soil Cd [μg kg^{-1}]	84.1 ± 11.8 (a)	76.4 ± 7.9 (a, b)	50.1 ± 7.6 (b)	**($p = 0.08$)**
Available: total soil Cd [%]	22.9 ± 1.8	23.5 ± 1.6	23.8 ± 3.1	$p = 0.95$
Available Cd: CEC [μg $cmol+^{-1}$]	3.9 ± 0.3	3.3 ± 0.2	2.9 ± 0.5	**($p = 0.1$)**
Grain Cd [μg kg^{-1}]	34.6 ± 4	28.9 ± 2.6	29.6 ± 2.7	$p = 0.43^{\ddagger}$
Grain Cd: grain N [ppm]	1.9 ± 0.2	1.7 ± 0.1	1.6 ± 0.2	$p = 0.58^{\S}$

Including the nested effect of cultivar within system resulted in a better fit for †system $p = 0.0005$ with system:cultivar $p = 0.006$; ‡system $p = 0.2$ with system:cultivar $p = 0.03$; §system $p = 0.42$ with system:cultivar $p = 0.06$.

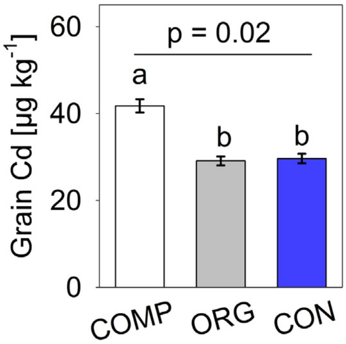

Fig. 2. Grain Cd of farming systems with only farms with livestock included. Three farming systems were investigated including 6 organic farms with compost use (COMP), 8 organic farms without compost use (ORG), and 6 conventional farms without compost use (CON). When including the nested effect of cultivar within system, the system effect was $p = 0.015$ and the nested system:cultivar effect was $p = 0.052$.

extractable soil Cd, while they did not correlate with DTPA-extractable soil Zn although pH did (Fig. 4; Table 3a). The clay content was positively correlated to total soil Cd and had a similar tendency to correlate with total soil Zn, whereas for both soil Cd and Zn the correlation coefficient was in a similar range or higher for SOC and CEC than for clay content (Table 3a). The soil properties were positively correlated with each other except soil pH (Table 3a). All other soil properties including grain yield did not show correlations with grain Zn and Cd concentrations (Table 3a).

The different Zn concentrations were not correlated significantly with each other (Table 3b). However, the total soil Cd concentration was correlated with both the DTPA-extractable soil and grain Cd, although DTPA-extractable soil and grain Cd were not correlated (Table 3c). The Zn concentrations correlated positively with the Cd concentrations: total soil concentrations ($p = 0.01$; $r = 0.54$), DTPA-extractable soil concentrations ($p = 0.001$; $r = 0.60$), and grain concentrations ($p = 0.01$; $r = 0.53$).

4. Discussion

4.1. Soil concentrations of Zn and Cd

The positive correlations of total soil Zn and Cd with SOC concentration and CEC suggest that organic matter was a major factor in providing binding capacity for Zn and Cd retention in the analysed agricultural fields, which is in line with previous sorption experiments (Lair et al., 2006). The clay content also correlated positively with CEC but had a lower correlation coefficient with total soil Zn and Cd so the clay content was probably less important for total soil Zn and Cd than organic matter. The positive correlation of SOC with total soil Zn and Cd may also be due to the higher Zn and Cd inputs through manure additions containing high concentrations of Zn and Cd from feed additives (Belon et al., 2012; Nicholson et al., 1999; Oliver et al., 1993).

Consequently, organic farms with compost use had higher SOC concentrations than on the conventional farms and higher total and available soil Cd concentrations than on conventional ones. The total and available soil Cd on organic farms without compost use were in between compost and conventional farms. This suggests a higher Cd binding and availability on the organic farms, which could be explained by higher organic matter concentrations according to the positive correlations of total and available Cd with SOC and CEC. The organic compost farms showed a higher ratio of total and available soil Cd concentration to CEC than the conventional farms suggesting that the increased total soil Cd concentration on compost farms exceeded the binding capacity of the SOM and could not be completely bound therefore leading to increased available Cd. This is in contrast to a study by Haghiri (1974) who observed a retention of Cd and a decrease of its availability through binding to organic matter. Narwal and Singh (1998) found that the application of cow manure reduced the exchangeable and DTPA-extractable Cd concentrations in the soil. However, both studies were

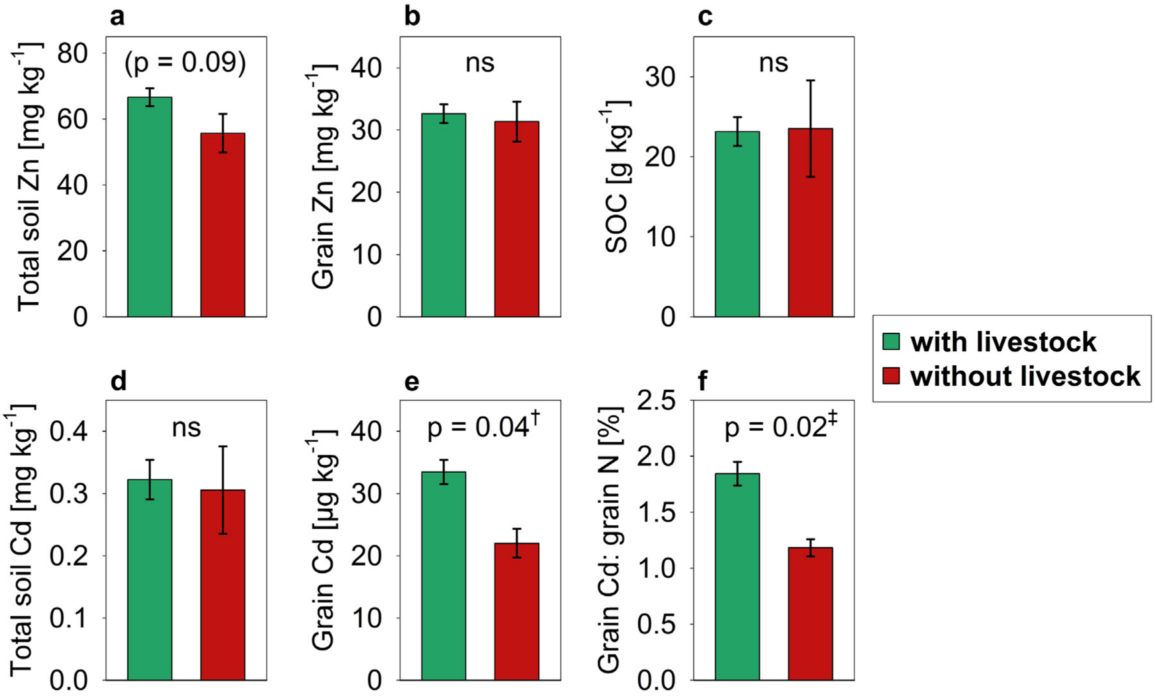

Fig. 3. Comparison of farms over all three farming systems with and without livestock with reference to (a) total soil Zn, (b) grain Zn, (c) soil organic carbon, (d) total soil Cd, (e) grain Cd, and (f) grain Cd: grain N. Of the 28 investigated farms, 22 farms included livestock production and 6 produced no livestock. Including the nested effect of cultivar within system resulted in a better fit in (e) with †livestock $p = 0.008$ with livestock:cultivar $p = 0.047$ and (f) with ‡livestock $p = 0.01$ with livestock:cultivar $p = 0.1$.

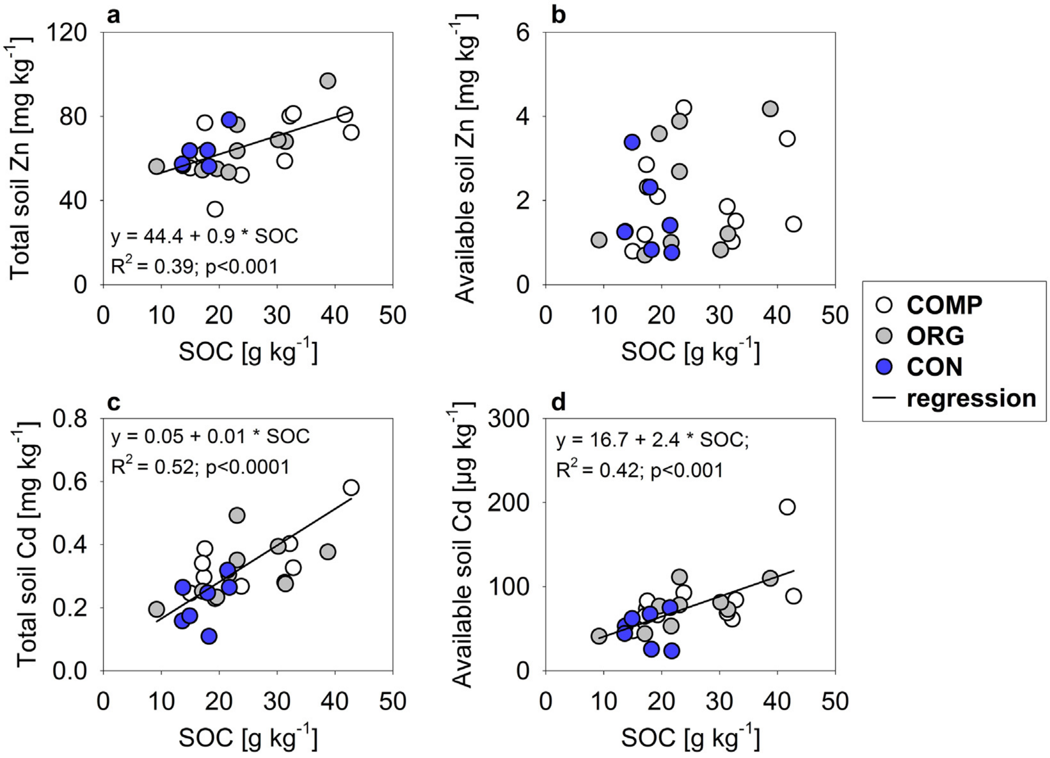

Fig. 4. Linear regressions of soil organic carbon (SOC) with (a) total and (b) available soil Zn and (c) total and (d) available soil Cd. Three farming systems were investigated including 11 organic farms with compost use (COMP), 10 organic farms without compost use (ORG), and 7 conventional farms without compost use (CON).

Table 3
Correlation matrices of soil and grain Zn and Cd concentrations (a) with various soil properties and relationships of these soil properties with each other, (b) Zn concentrations with each other and (c) Cd concentrations with each other.

a

	Clay content	CEC	pH	SOC conc.
Zn				
Total soil Zn	**(p = 0.06 r = 0.37)**	**p < 0.01 r = 0.52**	p = 0.30 r = −0.21	**p < 0.001**[*] **r = 0.63**
Available soil Zn	p = 0.73 r = −0.07	p = 0.49 r = 0.14	**p = 0.02 r = 0.43**	p = 0.30[*] r = 0.21
Grain Zn	p = 0.52 r = 0.13	p = 0.40 r = 0.17	p = 0.90 r = −0.02	p = 0.54 r = 0.12
Cd				
Total soil Cd	**p < 0.001 r = 0.60**	**p < 0.0001 r = 0.70**	p = 0.50 r = 0.13	**p < 0.0001**[*] **r = 0.72**
Available soil Cd	p = 0.83 r = 0.42	**p < 0.001 r = 0.61**	p = 0.26 r = 0.22	**p < 0.001**[*] **r = 0.65**
Grain Cd	p = 0.16 r = 0.29	p = 0.32 r = 0.20	p = 0.35 r = −0.19	p = 0.29 r = 0.22
Clay content		**p < 0.0001 r = 0.81**	**p = 0.01 r = 0.47**	**p < 0.01 r = 0.53**
CEC			**p = 0.04 r = 0.39**	**p < 0.0001 r = 0.84**
pH				p = 0.87 r = 0.03

[*] Linear regressions of these relationships are shown in Fig. 4.

b

	Available soil Zn	Grain Zn
Total soil Zn	p = 0.34 r = 0.19	p = 0.17 r = 0.27
Available soil Zn		p = 0.76 r = 0.06

c

	Available soil Cd	Grain Cd
Total soil Cd	**p < 0.0001 r = 0.85**	**p = 0.03 r = 0.42**
Available soil Cd		p = 0.18 r = 0.27

P-values are displayed in bold when p < 0.05 and in bold and brackets when p ≤ 0.1.

done on soils with a higher inherent Cd contamination and probably did not add Cd with the organic matter. Batch adsorption experiments demonstrated that organic matter can immobilise Cd which showed a higher affinity for organic surfaces than Zn (Elliott et al., 1986; Lair et al., 2007a). However, the mobilisation through the release of chelating agents from organic matter also seems to play a role. Previous studies suggested that the formation of dissolved organic ligands and amino acids during the decomposition of organic matter facilitate a higher bioavailability of metals through their chelation (Aghili et al., 2014; Bolan et al., 2004; Habiby et al., 2014). The formation of chelating agents seems to increase Cd availability on the organic farms of this study, especially on those with compost use. The available Cd concentrations in our study were not related to soil pH. As available soil Cd and grain Cd were both related to total soil Cd, we concluded that an increased Cd input with organic matter, that remains partly available, leads to a high grain uptake of Cd. The effect of organic matter was confirmed by a recent study in a comparable environment that concluded that the availability of Cd measured with DTPA extraction was governed more by farmyard manure input than by mineral soil N or pH (Grüter et al., 2017).

In contrast to soil Cd, we did not find significant evidence for the hypothesised increase of soil Zn concentrations on organic farms with or without compost use, despite their raised SOC concentrations compared to conventional farms. The positive correlation of total soil Zn with SOC indicates a general increase of Zn binding independent from the specific farming system. Unlike Cd, the available Zn was not correlated to clay content, SOC, or CEC. Instead, DTPA-extractable Zn was positively correlated with soil pH, which did not vary between the farming systems in our study. A positive correlation of DTPA-extractable Zn with soil pH contradicts previous reports and suggests that DTPA extracts included also calcium carbonate bound Zn that is less soluble. The observed impact of SOC on available soil Cd, but not on available soil Zn, is in contrast to previous studies that found combined effects for both elements upon manure addition (Baldantoni et al., 2010; Benke et al., 2008; Grüter et al., 2017). Under the agricultural field conditions of our study, higher total soil Zn based on increased binding capacities due to more organic matter did not translate into more available or grain Zn. It appears that soil Zn binds more strongly to organic matter than Cd. Previous studies have shown that soil Cd has a higher mobility than Zn because Cd is predominantly present in acid-soluble fractions (Anju and Banerjee, 2011; Ming et al., 2016).

In addition, most of the farms in our study produced cattle which could have led to Zn inputs with manure of around 700 g Zn ha^{-1} according to Nicholson et al. (1999). In fact, increasing Zn contents in agricultural soils of Switzerland during the past 20 years have been attributed to increasingly intensive livestock production and management of grassland (Gubler et al., 2015). This trend explains the observed tendency in our study towards higher total soil Zn in the farms with livestock than in those without. This means that soil Zn is mainly influenced by multiple factors like livestock production and organic matter whereas the availability of soil Zn seems to depend on other factors than the farming system, SOC concentration, or livestock production in the uncontaminated agricultural soils of our research site.

4.2. Wheat grain uptake of Zn and Cd

Despite the elevated available soil Cd contents in organic farms with compost use, these did not lead to significantly higher grain Cd compared to conventional farms. The higher available Cd could be retained in the soil and grain uptake was prevented as shown by a Cd isotope fractionation study, that highlighted plant mechanisms to avoid the accumulation of Cd (Wiggenhauser et al., 2016). If compared only across the farms with livestock, the organic farms with compost use showed a higher grain Cd than in other farming systems. When comparing farms with and without livestock production, we found no significant difference in the soil Cd or SOC concentration. This means that binding sites provided by SOC do not explain the difference in grain Cd between farms with and without livestock production. Instead, livestock production could have led to an input of Cd that was taken up by the wheat grains. A previous study showed that recently added Zn and Cd ions can remain mobile and could, thus, be taken up by wheat grains (Lair et al., 2007a). The relationship of livestock production with soil Cd was demonstrated in a previous study on the Cd in agricultural soils of England where manure application from cattle production added 3 g Cd ha^{-1} to soils (Nicholson et al., 1999). Especially mineral feed supplements represent a major input pathway of Cd into agricultural soils (Lindén et al., 2003). As the use of cattle manure was probably higher in the farms with livestock, the Cd input through cattle manure might be responsible for a higher grain Cd uptake. This might depend on the specific composition and Cd contamination of the manure. An analysis of compost mixtures in Switzerland showed a high variability of Cd content but did not include compost containing manure (Kupper et al., 2014).

The wheat grain yield was higher on conventional farms than on organic farms whereas the grain N concentration was similar for all analysed farming systems. A higher ratio of grain Zn to grain N concentration on organic farms than on conventional farms indicated a dilution of Zn in the increased biomass of the conventional farms (Cakmak and Kutman, 2017) and this was also influenced by cultivar as can be seen when including it as a nested effect within the system effect (Table 2). Accordingly, the grain Zn concentration of conventional farms was lowest, but there was no significant difference between the farming systems. Furthermore, in the conventional farms a higher N_{min} input over the crop rotation and during the wheat year could have enhanced the mobilisation of Zn towards the grain and might have increased the grain uptake of Zn, compensating for the effect of increased organic matter management in the other treatments (Erenoglu et al., 2011; Kutman et al., 2011; Lorenz et al., 1994). However, the grain Zn in our study (32.4 mg kg^{-1}) was below the values of a research trial in a comparable environment (Grüter et al., 2017) demonstrating that other factors affect the Zn uptake by wheat grains under agricultural field conditions. The grain Zn concentrations of our study are in agreement with a previous study in Switzerland that detected no significant difference in grain Zn concentration between organic and conventional farms (Mäder et al., 2007). The nested effect of cultivar was important in explaining grain Zn and Cd uptake differences between the farming systems and their relationships with the grain N uptake. Previous studies also found cultivar-specific effects and linked these with different internal allocation of Cd within the plant (Shi et al., 2015). The genotypic differences in grain Cd concentrations were shown to vary to a higher degree and were more significantly correlated with grain N than Zn (Gao et al., 2011). In our study, the farms with livestock production indicated more grain Cd than those without which was also partially explained by the nested cultivar effect. Therefore, depending on farm system and livestock production, the nested impact of wheat cultivar could be related to a combined genotype-environment effect in N uptake.

Interestingly, total soil Zn was higher with livestock than without, but that difference did not translate obviously into grain Zn. Previous studies suggested that the Zn transport mechanism within plants can have a higher affinity for Cd when both metals co-occur (Hart et al., 2002; Shute and Macfie, 2006). In this study, we found combined effects for both elements in soil and grain. However, grain Zn did not correlate with total or available soil Zn and, thus, grain Zn uptake appears to be determined by more than the soil properties. Instead, plants can preferably regulate Zn homeostasis while regulating Cd to a lower extent (Clemens, 2001; Grüter et al., 2017; Hacisalihoglu and Kochian, 2003).

Besides considering cattle manure as a potential source of metals, the recycling or biocycling of crop residues for feeding and successive excretion in livestock manure, which was applied as fertiliser on organic farms with and without compost use, may also lead to an on-going accumulation of metals. Such a relationship was reported in an analysis of a 7 yr long-term field trial in Sweden indicating higher Cd soil contents if crop residues were returned to the soil instead of being removed (Andersson and Siman, 1991). Biocycling might be specifically high on organic farms due to their high C input and a residual accumulation of Zn and Cd during composting, increasing soil Cd (Moulis and Thévenod, 2010). On the other hand, the higher grain yield and lower biocycling on the conventional farms might lead to a larger removal flux.

5. Conclusion

Organic matter mainly mediated the soil Zn and Cd concentrations in the analysed Swiss wheat farms. Accordingly, organic farms with compost use with a raised SOC concentration and CEC revealed higher soil and grain Cd contents than conventional farms explained by a combination of compost application, livestock production, and a cultivar effect. This increased Cd binding sites, biocycling of Cd within the farm and potentially also available Cd inputs that were taken up by wheat grain. The soil Zn concentrations were not significantly different across the farming systems probably due a stronger binding of soil Zn to organic matter, warranting further investigation. Furthermore, livestock production increased soil Zn due to Zn supplementation in animal feed subsequently supplied to the soils in manure. The grain Zn concentrations were decoupled from soil Zn and were in a similar range in all farming systems indicating that the analysed farming systems were not effective in increasing grain Zn. The cultivar effect nested in system and livestock production effects could explain grain Cd uptake and its relationship with the grain N uptake indicating a substantial genotype-environment effect. Future studies are needed to analyse real farm environments to gain further understanding about the complexity of supplemented livestock production systems, potentially contaminated fertilisers, differing soil properties and management factors like biocycling. Our study underlines the importance of Zn and Cd monitoring in agricultural soils to detect contamination and evaluate management strategies to increase Zn as a required trace element and reduce Cd pollution in farming systems. A reduction of Cd within organic farming systems with compost use will be necessary to limit the accumulation of Cd in the long-term.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2018.05.187.

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