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ORIGINAL ARTICLE

Trace element concentrations in cereal grain of long-term field trials with organic fertilizer in Sweden

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Abstract Long-term use of organic fertilizers can lead to slow accumulation of trace elements in arable soil, whereas cropping systems with no return of organic residues to soil can lead to depletion. These changes in soil concentrations may potentially influence crop uptake of both essential and toxic metals over time. The aim of this study was to investigate the long-term use of manure and sewage sludge on trace element composition of cereal grain samples from ongoing field experiments. The analyses showed that the organic fertilizers had limited or no impact on grain concentrations of cadmium (Cd), copper (Cu), manganese (Mn), molybdenum (Mo) and selenium (Se). Concentrations of these metals in grain remained low to moderate. However, application of the organic residues resulted in higher grain concentrations of zinc (Zn) at several locations, although results for different sites were contradictory. It was concluded that added trace metals present in organic fertilizer are not easily available to crops and that changes in soil properties, such as pH, and root proliferation often are of greater importance for crop uptake. Application of sewage sludge with a low Cd content to agricultural soil does not pose a high risk of increased Cd concentrations in crops. At low Cd concentrations as in Swedish arable soils, the Cd:Zn ratio seems to have little importance at low to moderate input of Cd and Zn.

Keywords Manure · Micronutrients · Phytoavailability · Sewage sludge · Spring barley · Winter wheat

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Introduction

During the last 50 years, there has been a differentiation in agriculture into farms with or without animal husbandry. Crop production without animals is often characterized by large inputs of mineral fertilizer, no addition of organic material and low inputs of trace elements. This may lead to slow depletion of essential trace elements in arable soils on farms without animals which could increase the risk of micronutrient deficiency and reduced yield as well as decreased quality of food crops for human consumption. Several studies have reported declining trace element concentrations in crops over recent decades (Ekholm et al. 2007; Kirchmann et al. 2009). Depletion of trace elements in soil, together with high usage of NPK fertilizers, has been suggested as one possible explanation for this decline (Thomas 2003).

The application of sewage sludge to arable soils on crop production farms can be an alternative to manure addition, providing both organic matter and nutrients. The supply of essential trace elements with sewage sludge can be positive for yield and crop quality, but also raises concerns about unwanted metals such as cadmium (Cd) added with sludge accumulating in soils and crops in the long run (McBride 1995). Even though heavy metal concentrations in Swedish sewage sludge have declined over the years (Kärrman et al. 2007), application of sewage sludge can still cause an accumulation in soil. Also essential metals such as copper (Cu) and zinc (Zn) can accumulate in soil when sewage sludge or manure is applied on a regular basis. These metals are used as animal feed additives, ending up in manure, and are also enriched during sewage treatment.

The effects of organic fertilizers on trace element concentrations in crops are inconsistent. This inconsistency can be due to: (1) Variable metal concentrations in the organic amendments applied, (2) different application rates, (3) single or long-term application, (4) different impact on soil properties (pH, redox potential, organic matter content) influencing crop uptake and (5) high native soil metal concentrations overshadowing the impact of metals added with organic fertilizers.

Organic amendments are diverse products in terms of composition and properties. Some previous studies have used products with very high trace element concentrations or at extremely large quantities (Hooda et al. 1997; Granato et al. 2004; Evanylo et al. 2006). Others have conducted the studies under conditions differing from the current study in term of physical properties of the amendment used or by applying it to a tropical soil with different properties than soils in temperate regions (Bartl et al. 2002; Li et al. 2007; Nogueira et al. 2013). However, studies with moderate application rates of amendments, which are most relevant for common agricultural practices, also show contrasting results. Some indicate increased uptake of some trace metals (Pascual et al. 2004; Marcato et al. 2009; Codling 2014), whereas others show no significant differences or even a decline in metals upon application of organic amendments compared with mineral fertilizer or unfertilized controls (Andersson 1976; Hanc et al. 2008; Singh et al. 2010).

Total element concentration in soil is a poor indicator of crop uptake, whereas phytoavailability of metals in organic amendments is a key variable enabling prediction of uptake by crops and assessment of the environmental risks of potentially toxic elements. One way to assess the phytoavailability of metals in soil is through the ratio between crop and soil concentrations of a certain element (Heemsbergen et al. 2010), i.e., the bio-concentration factor (BCF). The approach allows an assessment of the potential benefit/risk of organic amendments.

The aims of the present study were to investigate the impact of organic fertilizers on concentrations of micronutrients and non-essential trace elements in cereal crops and to evaluate the phytoavailability of metals in sewage sludge. The specific objective was to determine how long-term application of organic fertilizers, compared with mineral fertilizer or no fertilizer, affected metal concentrations in cereals. The starting hypothesis was that long-term application of organic fertilizer increases the concentrations of some, but not all, trace metals in grain. However, as trace metals have different properties, the following five specific sub-hypotheses were formulated:

1. Selenium (Se) in organic fertilizers is mainly present in organic forms. When organic matter decays, Se is mineralized to selenite and selenate. The potential amount of Se mineralized from organic amendments can be high enough to influence crop composition.
2. Copper (Cu) is strongly bound to organic matter. Even when organic matter decomposes and Cu is released, there are still a large number of binding sites available for Cu to re-bind. Addition of organic fertilizers will therefore not significantly affect Cu concentrations in crops.
3. Manganese (Mn) is abundant in soils and plant availability is mainly controlled by soil pH and redox conditions. Fertilization with organic amendments will not alter crop uptake, unless pH and redox are affected.
4. Crop availability of molybdenum (Mo) is mainly affected by pH values in soil. As addition of Mo with organic fertilizers usually is small, there will be no effect of organic fertilizer unless soil pH is affected.
5. Cadmium (Cd) and zinc (Zn) are easily plant available metals in soil and have similar chemical behaviour. Adding these metals in organic fertilizers will increase the concentrations of Cd and Zn in crops. In addition, competition between Cd and Zn may affect Cd uptake by crops. At increasing

Cd:Zn ratios in organic amendments or in soil, higher Cd concentrations in crops can be expected.

Materials and methods

Experimental sites and amendments

The effects of different fertilizer treatments on the concentrations of trace elements in soil and cereal grain were investigated using existing long-term field trials in Sweden. Soil characteristics for the included experimental sites are shown in Table 1. Different organic fertilizers such as sewage sludge and manure were used at the different sites. Trace element concentrations for the amendments used were not analysed on a regular basis, and instead mean concentrations for organic fertilizers in Sweden are presented and used for balance calculations (Steineck et al. 1999), (Table 2). Yearly amounts of metals added to soil met Swedish regulations except for high rates of sewage sludge added at the Lanna and Petersborg site. A short description of the different sites and treatments is given in subsequent paragraphs.

Lanna site

The on-going trial at Lanna research station in south-west Sweden (58°21 N, 13°08E) was started in 1996 to study the effect of different organic amendments and N fertilizers on soil organic matter content, soil biological properties and crop yield. The soil is a silty clay (42 % clay) and the experiment has a randomized block design with four replicate plots per treatment and with each plot measuring 8 m × 14 m. The treatments chosen for the present study were: (A) No fertilization; (B) $Ca(NO_3)_2$ at 80 kg N ha^{-1} $year^{-1}$ plus single superphosphate at a rate of 40 kg P and 30 kg K as KCl every 2 years; (C) $(NH_4)_2SO_4$ at 80 kg N ha^{-1} $year^{-1}$ and PK as in B; (D) cattle solid manure at 8 Mg dm ha^{-1} every 2 years; and (E) sewage sludge at 8 Mg dm ha^{-1} every 2 years. The crop rotation consists of oats, spring barley and winter wheat. Grain samples of winter wheat (*Triticum aestivum*) and topsoil samples (0–20 cm) were collected in 2010 and analyzed.

Petersborg site

The trial at Petersborg in southern Sweden (55°42 N, 14°13E) was started in 1981 to test the impact of sewage sludge addition on soil and crop properties. The soil is a sandy loam (14 % clay). Data from the following treatments were used to evaluate the effect of sewage sludge on trace element concentration in grains: (A) No fertilization; (B) sewage sludge at 4 Mg dm ha^{-1} every 4 years; (C) sewage sludge at 12 Mg dm ha^{-1} every 4 years; (D) mineral fertilizer with 140 kg N as $Ca(NO_3)_2$, 18 kg P (single

Table 1 Selected soil properties of the experimental sites

Experimental site	Soil texture	Clay content in topsoil (%)	Org C in topsoil (%)	pH in topsoil at start (H_2O)
Lanna	Silty clay	42	2.0	6.7
Petersborg	Sandy loam	14	1.2	6.8
Mellby	Loamy sand	6	2.6	6.0
Ekebo	Sandy loam	14	3.1	6.8
Orup	Sandy loam	13	2.4	6.2
S:a Ugglarp	Silty loam	8	1.5	6.6
Fjärdingslöv	Sandy loam	17	1.4	7.5
Örja	Sandy clay loam	15	1.1	7.2
Bjertorp	Silty clay	30	2.2	6.4
Vreta Kloster	Silty clay	50	2.1	6.7
Högåsa	Silty sand	10	2.4	5.9
Kungsängen	Gyttja clay (acid sulphate clay)	56	2.1	7.1

Measurements were made at the start of each experiment

Table 2 Trace element concentrations in organic fertilizers in Sweden (mean ± SD) and maximum addition of metals with sewage sludge according to Swedish regulations (SNFS 1994: 2)

Element	Trace element concentration (mg kg^{-1} dm)				
	Cattle solid manure (n = 17)	Cattle slurry (n = 15)	Pig slurry (n = 14)	Sewage sludge (n = 48)	Maximum addition with sewage sludge (g ha^{-1} $year^{-1}$)
Cd	0.16 ± 0.07	0.13 ± 0.05	0.17 ± 0.08	1.4 ± 1.5	0.75
Cu	31 ± 8	49 ± 42	178 ± 40	390 ± 300	300
Mn	230 ± 32	247 ± 78	302 ± 63	280 ± 220	No regulation
Mo	No data	4.5	4.9	6.7 ± 3.5	–
Se	0.6 ± 0.3	0.7 ± 0.2	1.6 ± 0.5	1.3 ± 0.5	–
Zn	174 ± 32	190 ± 41	635 ± 153	550 ± 320	600

Data from national surveys (Steineck et al. 1999; Eriksson 2001)

superphosphate) and 63 kg K as PK fertilizer; and (E) sewage sludge (treatment C) plus mineral fertilizer (treatment D). The experiment has a randomized block design with four replicate plots in each treatment and with plot size 6 m × 20 m. The crop rotation consists of winter wheat, sugar beet, spring barley and oilseed rape. Grain samples of winter wheat (*Triticum aestivum*) and topsoil samples (0–20 cm) were collected in 2010 and analyzed.

Mellby site

The Mellby experimental site is situated in south-west Sweden (56°29 N, 13°00E) on a sandy loam. The experiment started in 1989 with the aim of investigating the effects of catch crops and manure addition on nitrogen leaching (Torstensson and Aronsson 2000). Plot size is 30 m × 30 m and there are three replicates per treatment (unfertilized control has one replicate). Treatments used in this study were: (A) No fertilization; (B) mineral nitrogen at 90 kg N ha^{-1} $year^{-1}$ as NH_4NO_3 and (C) pig slurry at 113 kg tot-N ha^{-1} $year^{-1}$ + mineral nitrogen at 45 kg ha^{-1} $year^{-1}$. Grain samples of spring barley (*Hordeum vulgare*) from 2010 to 2013 were collected and analyzed.

Long-term soil fertility experiments

The Swedish long-term soil fertility experiments started between 1956 and 1966 and are running at 10 different sites in southern and central Sweden. In this study, archived wheat grain samples taken from nine sites over 3 years between 1995 and 2003 were analyzed. The treatments included: (A) No fertilization, (B) mineral fertilization with 80 kg N as calcium ammonium nitrate, 30 kg P as single superphosphate and 60 kg K ha^{-1} $year^{-1}$ as KCl; (C) cattle manure at 25 Mg fresh weight ha^{-1} every 4 years; and (D) mineral fertilizer plus cattle manure (treatment B + C). The crop rotation in treatments A and B consists of spring barley, oilseed rape, winter wheat and sugar beet (southern sites)/oats (northern sites), while in treatments C and D oilseed rape is replaced by ley. Since only one pooled sample from each year was available, three different years between 1995 and 2003 were used as replicates and grain samples of winter wheat (*Triticum aestivum*) were analyzed.

Soil and grain analysis

Grain samples were digested in concentrated nitric acid (HNO_3) and trace element concentrations were determined by inductively coupled plasma mass spectrometry (ICP-MS; Elan 6100 ACP-MS; Perkin Elmer SCIEX instruments). Whole grains were used to avoid contamination at milling. The elements analyzed were cadmium (Cd), copper (Cu), manganese (Mn), molybdenum (Mo), selenium (Se) and zinc (Zn). At harvest, one sample from each replicate plot was collected and analysed. For some selected sites, dried (oven-dried at 40 °C) and sieved soil samples (<2 mm) were digested in concentrated nitric acid (HNO_3) and analyzed for trace metal contents (ICP-MS). Soil samples were collected using a soil auger (0–20 cm) and 10 subsamples from each replicate plot were merged to one pooled sample for each treatment and analyzed. Soil pH measurements was made in water (H_2O) with a soil:water ratio of 1:5. All metal concentrations are expressed on a dry matter basis.

Bio-concentration factors

Bio-concentration factors were calculated using data from the Lanna and Petersborg trials to evaluate the relative phytoavailability of trace elements in sewage sludge. The BCF values were obtained by dividing crop metal concentration (mg kg^{-1}) by total soil metal concentration (mg kg^{-1}) for each element (Heemsbergen et al. 2010).

Statistical analysis

The statistical analysis for comparison between treatments was made using one-way ANOVA in JMP 9 (SAS Institute Inc., Cary, NC, USA). Graphs were prepared using SigmaPlot 12.3 (Systat Software Inc., San Jose, CA, USA). Error bars in figures indicate standard deviation.

Results and discussion

Results from the long-term field trials are presented and discussed separately below for each element. The dataset of grain concentrations, soil properties and crop yields is presented in an electronic supplementary data set (Online Resource 1).

Cadmium

Cadmium concentration in wheat grain from Lanna, Petersborg and nine soil fertility experiments varied between 0.019 and 0.081 mg kg^{-1}, which is within the range reported for Swedish winter wheat (Eriksson et al. 2010). Even in the spiked Cd treatment, crop Cd concentrations were below the maximum limit for cereal grain of 0.1 mg Cd kg^{-1} (EC 1881/2006).

At most sites, there were no differences between any of the treatments. At Lanna, application of cattle manure resulted in significantly lower Cd concentrations in wheat grains than fertilization with $(NH_4)_2SO_4$. However, this difference can probably be attributed to pH differences, since the $(NH_4)_2SO_4$ treatment resulted in a lower soil pH (by 0.4 U) than the manure treatment. The Cd concentration in crops in the $Ca(NO_3)_2$ and manure treatments did not differ and soils in these treatments had similar pH values.

Treatment with 20 kg P ha^{-1} $year^{-1}$ as mineral fertilizer corresponded to Cd addition of 320 mg Cd ha^{-1} $year^{-1}$, assuming a mean Cd concentration of 16 mg Cd kg^{-1} P (Eriksson 2001). The amount of Cd applied with manure was approximately 200-600 mg Cd ha^{-1} $year^{-1}$ (mean Cd concentration 12 mg Cd kg^{-1} P) and the amount applied with sewage sludge was approximately 5-6 g Cd ha^{-1} $year^{-1}$ (mean Cd concentration 44 mg kg^{-1} P), (Eriksson 2001). Despite the net input of Cd with organic fertilizers amounting to 10–100 g over the years, concentrations of Cd in crops did not increase in these treatments. However, soil treatment with additional water-soluble Cd salts (about 50 g Cd ha^{-1} $year^{-1}$) together with sewage sludge resulted in a higher crop Cd concentration (0.059 mg kg^{-1}) than sewage sludge addition only (0.026 mg kg^{-1}). Similar results of increased crop uptake after addition of metal salts have been found for nickel (Ni) in the same field trials (Hamnér et al. 2013). Soil Cd concentrations in this study were overall low and varied between 0.12 and 0.29 mg kg^{-1}, being lower than those reported to cause phytotoxicity and the acceptable limit for arable soil in Europe (2.3 mg Cd kg^{-1} soil), (Smolders and Mertens 2013). At these low Cd soil concentrations one would expect an increased crop uptake at increased soil concentrations since there is no reason for the plant to inhibit root uptake. The element can thereby escape the ‘plant barrier’ that can otherwise prevent elements reaching the shoot and grain of crops (Basta et al. 2005; Chaney 2012). This could also be shown in this study where a higher total concentration of Cd resulted in higher Cd grain concentrations (Fig. 1a). An important factor that also may influence plant Cd concentration is the competition between Cd and Zn during root uptake (e.g., Chaney 2015). Data from this study showed that a higher Cd:Zn ratio in the Cd spiked treatment at Lanna resulted in a higher Cd concentration in grain (Fig. 1b). However, at Petersborg, a change in the Cd:Zn ratio through fertilization with sewage sludge did not affect grain Cd concentration. Overall low Cd concentrations in the soils and small changes in the Cd:Zn ratio compared to other studies (Chaney 2015) may be the reason for unaffected crop Cd concentrations.

There are concerns that concentrations of Cd and other toxic metals may increase in crops when metals

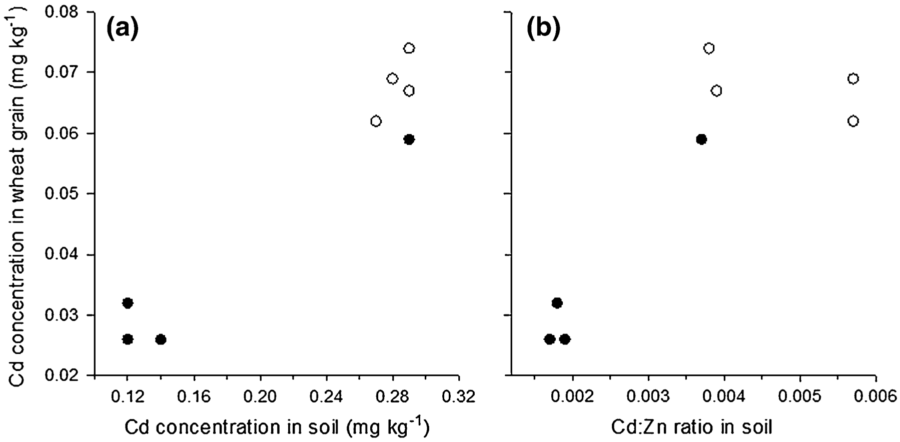

Fig. 1 Cadmium (Cd) concentrations in wheat grain in response to **a** Cd concentration in soil and **b** Cd:Zn ratio in soil (n = 8). *Filled symbols* = Lanna site, *open symbols* = Petersborg site

have been enriched in soil through long-term sewage sludge application, especially when application stops and metals are released during decay of the organic matter. This has been described as the "sludge time bomb theory" (McBride 1995). However, studies on soils with high Cd concentrations have not corroborated this theory, as no increase in crop Cd concentrations was found even 10–20 years after the last addition of sewage sludge, probably because release of Cd bound to soil organic matter and Fe/Mn-oxides is very limited (Sukkariyah et al. 2005; Kukier et al. 2010). Considering that the Cd content in Swedish sewage sludge is low compared to many countries and that addition of Cd is strictly limited by Swedish regulations to a maximum of 0.75 g Cd ha^{-1} $year^{-1}$ (SNFS 1994: 2), the risk of increased crop Cd concentrations through use of sewage sludge can be considered low. Since other studies have shown that high Cd concentrations in sewage sludge increased Cd uptake by crops, keeping Cd concentrations low and having strict regulations for sewage treatment plants and applications to arable land is of importance to ensure crop quality.

At two soil fertility trial sites (Fjärdingslöv and Örja), application of mineral fertilizer combined with manure resulted in significantly higher crop Cd concentrations than mineral fertilizer alone. A similar trend was observed at three other locations, although differences were not significant. This finding is difficult to explain, since the amount of additional Cd added with manure was low, and since soil properties such as pH did not change significantly. One possible explanation is that soil organic matter content increased with manure applications which could increase metal mobility under certain conditions (Almås and Singh 2001).

The BCF values calculated for Cd at Lanna and Petersborg (Table 3) showed no differences between soil treatments. The amount of Cd added with sewage sludge was not high enough to cause a measurable accumulation in soil, but the results indicated that sewage sludge application did not affect Cd availability in soil compared with mineral fertilizer or native soil Cd. Only the treatment where sewage sludge had been spiked with water-soluble Cd caused a significantly higher soil Cd concentration, but still resulted in similar BCF values. Thus one can conclude that the relative plant availability of Cd was about the same for both the spiked Cd and treatments with only sewage sludge or mineral fertilizer.

Finally, our data did not support the hypothesis that organic fertilizer increases Cd concentrations in cereal grain.

Copper

Copper concentrations in grain varied between 1.74 and 4.80 mg Cu kg^{-1}, which is in the low to normal range. Addition of organic fertilizers resulted in a net input of Cu during the experimental period (15–30 years) of about 50 g for the low input of cattle manure up to 35 kg Cu for the highest sewage sludge

Table 3 Soil and grain concentrations and BCF-values of copper (Cu), zinc (Zn) and cadmium (Cd) at Lanna and Petersborg

Experimental sites and treatments	Cu conc. (mg kg^{-1})			Zn conc. (mg kg^{-1})			Cd conc. (mg kg^{-1})		
	Soil	Grain	BCF[a]	Soil	Grain	BCF[a]	Soil	Grain	BCF[a]
Lanna									
No fertilization	9.1	3.59	0.39	63	26.8	0.42	0.12	0.026	0.21
$Ca(NO_3)_2$ + PK	8.9	3.91	0.44	66	21.5	0.33	0.12	0.032	0.27
Sewage sludge	21	3.97	0.19	83	32.6	0.39	0.14	0.026	0.19
Sewage sludge + metals[b]	25	3.93	0.16	79	31.6	0.40	0.29	0.059	0.21
Petersborg									
No fertilization	10	3.95	0.40	47	28.0	0.60	0.27	0.062	0.23
$Ca(NO_3)_2$ + PK	10	3.05	0.31	49	25.0	0.51	0.28	0.069	0.25
Sewage sludge	21	4.18	0.20	74	26.8	0.36	0.29	0.067	0.23
Sewage sludge + NPK	22	3.88	0.18	77	32.3	0.42	0.29	0.074	0.26

[a] *BCF* Bioconcentration factor (element concentration in grain/element concentration in soil)

[b] Biennial addition of 3.04 kg Cu, 0.18 kg Zn and 0.1 kg Cd ha^{-1} as metal salts

treatment. At Lanna, cattle manure application caused no significant differences in grain Cu concentrations compared with $Ca(NO_3)_2$, but higher values were found in the $(NH_4)_2SO_4$ treatment, probably due to the lower soil pH caused by this fertilizer. Copper concentrations in grain after sewage sludge application did not differ from those receiving mineral fertilizer. At Petersborg, the Cu concentration in grains were not significantly different when mineral fertilizer was combined with sewage sludge than when mineral fertilizer was applied alone. This comparison is most relevant when evaluating the effect of the sewage sludge, since parameters other than fertilizer application were kept more or less constant. Similarly, at the Mellby site, there were no significant differences in grain Cu concentrations between the mineral fertilizer and the mineral fertilizer combined with pig slurry treatments.

Both at Lanna and Petersborg, treatments with sewage sludge had lower BCF values for Cu than the mineral-fertilized and unfertilized treatments (Table 3). This was due to increased soil concentration after sewage sludge application but unchanged crop Cu concentration. Even when $CuSO_4$ was applied at a rate of 3 kg Cu ha^{-1} together with sludge, which was ninefold more than the amount added with sewage sludge alone, grain Cu concentrations remained unaffected and no negative impact on yield was found. Moreover, a study by Kätterer et al. (2014) in the same field trial found no negative effects of Cu on microbial turnover in the Cu-spiked treatment.

Low phytoavailability of Cu after addition of organic amendments has also been found in other studies, indicating strong Cu adsorption (e.g., Bolan et al. 2003; Alva et al. 2005). Furthermore, several studies found that plant availability did not increase significantly over time in soils previously amended with sewage sludge or other organic manures (Oliver et al. 2005; Smolders et al. 2012; Codling 2014), rejecting the “sludge time bomb theory”.

At six out of nine sites for the long-term soil fertility experiments, there were no differences between treatments using animal manure and other treatments. At three sites (Ekebo, Orup and S:a Ugglarp), application of manure caused significantly higher crop Cu concentrations than use of mineral fertilizer (Fig. 2). However, combined application of mineral fertilizer and manure resulted in the same low crop Cu concentration as mineral fertilizer only, indicating that manure addition did not increase Cu availability in the soil. Instead, the most probable explanation is the large yield difference between the mineral fertilizer and manure treatments. The higher yields resulting from fertilizer use caused a dilution effect of Cu in the crop, as revealed by relatively low grain Cu concentrations (1.74–2.31 mg Cu kg^{-1}) in mineral-fertilized grain. An inadequate supply of Cu at these sites is a reasonable explanation. In fact, soils at these three

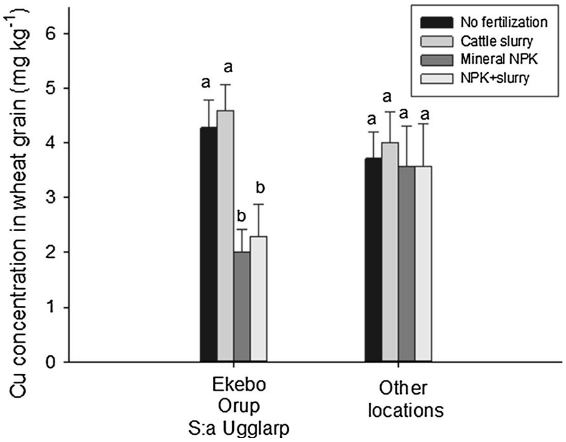

Fig. 2 Copper (Cu) concentrations in wheat grain in response to different fertilization treatments at Ekebo, Orup and S. Ugglarp compared to the other six long-term soil fertility sites. *Error bars* represent SD

sites are known to have natively dense subsoils (Kirchmann and Eriksson 1993; Kirchmann et al. 1996, 1999), resulting in poor root proliferation and low or no access to nutrients in the subsoil. In summary, our results showed that organic fertilizers do not increase grain Cu content.

Manganese

Concentrations of Mn in grain varied from 5.7 to 49.0 mg Mn kg^{-1}. Lowest crop concentrations (5.7–13.0 mg Mn kg^{-1}) measured at the Mellby site, indicated possible Mn deficiency. Manure application at this site did not increase Mn concentrations in grain despite limited supply by the soil. In general, different fertilizer treatments had no significant effect on Mn concentrations in grain at any of the sites.

The concentrations of Mn in Swedish manure and sewage sludge are lower (approximately 200–300 mg kg^{-1}) than mean native soil concentrations (450 mg kg^{-1}). Thus, addition of Mn through organic fertilizers may not be of significance for crop supply, an argument supported by the results of this study. It is known that phytoavailability of manganese in soil is mainly controlled by pH and redox potential and only when these factors are altered one can expect an impact of Mn concentration in crops. Potentially, addition of organic amendments can lower redox potential or influence soil pH but in our study this could not be confirmed.

There is one reservation, however, as Mn concentrations in grains are not a direct measure of Mn availability in soils. Only a limited proportion of Mn is translocated to the grain (Garnett and Graham 2005) and whole crop analysis is required for assessment of Mn uptake, which was not possible in this study.

Molybdenum

Molybdenum concentrations in grains ranged from 0.10 to 4.39 mg Mo kg^{-1}, showing very large differences between sites. Molybdenum concentrations in grain from Vreta Kloster were significantly higher than at other locations. Differences between sites could be attributed to low and high soil pH values. At Lanna, application of manure and $Ca(NO_3)_2$ resulted in significantly higher grain Mo concentrations than in crops treated with sewage sludge or $(NH_4)_2SO_4$. Corresponding soil pH values were also 0.5-0.6 units higher in the manure and $Ca(NO_3)_2$ treatments than in other treatments. The lowest Mo concentrations were found in crops fertilized with $(NH_4)_2SO_4$ (0.10 mg Mo kg^{-1}) illustrating the role of pH for Mo availability to crops. At the other long-term field sites, there were no significant differences in pH values between treatments.

At Fjärdingslöv, manure application resulted in significantly higher grain Mo concentrations compared to the other treatments, an effect that can possibly be attributed to manure application. However, the increased uptake could also be caused by high pH values in the subsoil at this site (Kirchmann et al. 1999). The manure treatment included ley in the crop rotation, which may have improved root proliferation of other crops and thereby improved access to trace elements in the subsoil.

As with manganese, Mo addition through organic fertilizers is often low. Thus, the indirect effect of fertilizer treatments on soil pH seems to determine Mo availability to crops, and not Mo addition with manure or sludge as such.

Selenium

Overall, crop Se concentrations were low, ranging from 0.014 to 0.106 mg Se kg^{-1}. The same low concentrations were found in the Swedish soil and crop monitoring programme, where on average 0.02 mg Se kg^{-1} was measured in wheat grain (data not published). Application of manure or sewage sludge did not increase the concentration of Se in grain at any site. At three sites, Se concentrations in crop samples were below the detection limit. Since the 1980s, cattle and sheep feed has been supplemented with Se compounds and thus cattle manures used at the sites were enriched with Se. Still, long-term application of cattle manure to soil did not increase Se concentrations in crops compared with other fertilizer treatments.

Several studies have reported low plant availability of Se in organic fertilizers (Ajwa et al. 1998; Gaskin et al. 2003) and strong retention of Se by soil organic matter (Johnsson 1991). Selenium is incorporated into organic matter in soil in a similar way as sulphur (S) and a positive correlation between soil organic matter and Se content has earlier been shown for Swedish soils (Shand et al. 2012). Therefore, decomposition of organic matter in soil seems to be a controlling factor for plant availability of Se. Application of animal manure has been proposed as a method to increase crop Se content in deficient soils (e.g., Kabata-Pendias 2001) and positive correlations between organic matter and Se uptake has been shown on mineral soils (Eich-Greatorex et al. 2007). However, results from our study showed no significant correlation between soil organic matter and crop Se concentrations (Fig. 3; $p = 0.77$). With application of organic fertilizers there is also an addition of sulphate which can compete with selenium at root uptake and thereby lower the impact on crop Se uptake. One can point out that the low Se concentrations in Swedish grain (and also in other crops in Sweden) may not be sufficient to meet the recommended daily Se intake level for humans (WHO 1996; NFA 2014). A similar situation existed in Finland until the 1980s (Alfthan et al. 2010), when controlled Se fertilization through mineral fertilizers was introduced.

Zinc

The Zn input through organic fertilizers over the years was between 5 kg (low input of cattle manure) and 45 kg (high input of sewage sludge). Grain Zn concentrations (19.9–42.3 mg Zn kg^{-1}) were significantly affected by application of organic fertilizers at several sites. At Lanna, addition of cattle manure resulted in significantly higher crop Zn concentrations than mineral fertilizer, while sewage sludge caused the highest Zn concentrations. At Mellby, Zn concentrations in grain increased after manure application, compared with mineral nitrogen application only, in one out of 2 years. In contrast, at two of the soil fertility experiments (S:a Ugglarp and Ekebo), application of manure resulted in lower crop Zn concentrations and at two other sites (Örja and Fjärdingslöv), combined manure and mineral fertilizer application led to lower Zn concentrations than mineral fertilizer only.

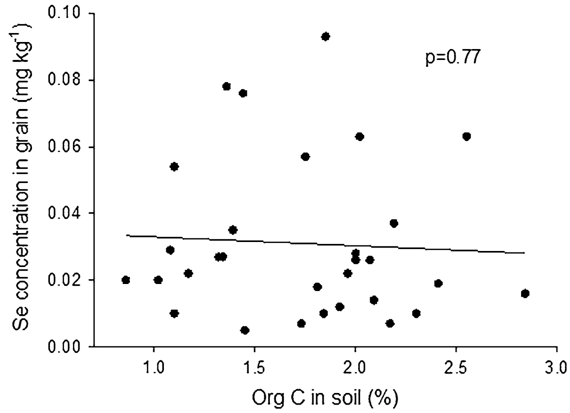

Fig. 3 Correlation between organic carbon in topsoil (%) and grain Se concentration (mg kg^{-1}) at nine sites of the Swedish long term fertility experiments (n = 30)

Inconsistent results can also be found in the literature, showing that soluble Zn concentrations in soil and Zn uptake in crops increased after sludge and manure application (Codling 2014; Gartler et al. 2013) or remained unaffected by addition of organic manure (e.g., Li et al. 2007). The reasons could be different plant availability in the amendments or soil Zn availability being altered by the organic amendments.

Calculation of BCF values for Zn showed no difference between sewage sludge and mineral fertilizer at Lanna, whereas at Petersborg sludge treatment decreased BCF values (Table 3). Soil and crop concentrations were similar at both sites. This indicates that phytoavailability of Zn in sewage sludge is not lower than that of native soil Zn. Moreover, the treatment with sewage sludge spiked with water-soluble $ZnSO_4$ resulted in similar BCF values. However, as the amount of Zn added as $ZnSO_4$ was small in comparison with the amount added with the sewage sludge, no significant differences between these treatments were expected. The results indicate that Zn added with organic materials is plant available to some extent and more mobile than other trace metals.

Conclusions

From the results of this study one can conclude the following:

- Even after long-term application (15–30 years) of different forms of manure and sewage sludge, there was limited or no impact of organic fertilizers on trace element concentrations in cereal grain, with the exception of Zn. Changes in soil properties caused by fertilization as well as root proliferation can be of greater importance for the phytoavailability of trace elements and crop uptake.
- Trace metals concentrations in crops are not affected by regular additions of organic manures when applied at rates being normal for Swedish agriculture. The risk of elevated crop concentrations of unwanted metals such as Cd through addition of sewage sludge is low due to low Cd concentrations in the sludge.
- At low soil Cd concentrations, the Cd:Zn ratio in soil has limited impact on crop uptake and is no better indicator than total Cd concentrations in soil.
- As no correlation was found between soil organic carbon in soil and grain Se, other Se sources such as air deposition must be considered to understand variations in Se crop uptake.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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