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An inventory of trace element inputs to agricultural soils in China

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ABSTRACT

It is important to understand the status and extent of soil contamination with trace elements to make sustainable management strategies for agricultural soils. The inputs of trace elements to agricultural soils via atmospheric deposition, livestock manures, fertilizers and agrochemicals, sewage irrigation and sewage sludge in China were analyzed and an annual inventory of trace element inputs was developed. The results showed that atmospheric deposition was responsible for 43–85% of the total As, Cr, Hg, Ni and Pb inputs, while livestock manures accounted for approximately 55%, 69% and 51% of the total Cd, Cu and Zn inputs, respectively. Among the elements concerned, Cd was a top priority in agricultural soils in China, with an average input rate of 0.004 mg/kg/yr in the plough layer (0–20 cm). Due to the spatial and temporal heterogeneity of the sources, the inventory as well as the environmental risks of trace elements in soils varies on a regional scale. For example, sewage sludge and fertilizers (mainly organic and phosphate-based inorganic fertilizers) can also be the predominant sources of trace elements where these materials were excessively applied. This work provides baseline information to develop policies to control and reduce toxic element inputs to and accumulation in agricultural soils.

1. Introduction

There has been a growing public concern over the potential accumulation of trace elements in agricultural soils in China owing to the rapid industrialization and urbanization and increasing reliance on chemicals in the last two decades. It has been estimated that contaminated soils result in a reduction of more than 1.0×10^7 tons of food supplies in China annually (Wei and Chen, 2001). Reducing inputs of toxic trace elements to soil has been a strategic aim for sustainable agriculture in China (State Council of PRC, 2005). However, the information on the status and extent of soil contamination with trace elements from different sources is still scarce and thus required for actions to be effectively targeted.

It is a challenging work to quantify the trace element inputs accurately since the sources and quantities are miscellaneous for different elements and the information is often scarce or incomplete on a national scale. Moreover, the characteristics of trace element inputs have been changing over time. For instance, sewage irrigation has caused a pollution area of about 3.6×10^6 hectares of agricultural land in China (Wang and Lin, 2003); however, with the increase in sewage disposal and the awareness of hazards of sewage irrigation, the environmental pressure from sewage irrigation has been significantly diminished in China. Meanwhile, electronic waste (e-waste) has become a main point source of trace element pollution in soils particularly in some areas in southern China in recent years (Wong et al., 2007). Therefore, a timely updated inventory of trace element inputs to agricultural soils is of great importance to assess the contribution of various sources to trace element inputs and their environmental risks posed by contaminated agricultural soils.

A comprehensive investigation on soil environmental quality on a national scale in China is being conducted collaboratively by the Ministry of Land and Resources and the State Environmental Protection Administration, aiming at identifying the status of soil contamination, introducing suitable environmental quality standards for soils and making decisions for remediation of contaminated soils. An elaborate analysis of the contribution of trace element sources will provide baseline information for the investigation and be of benefit to the environmental risk management of trace elements in agricultural soils. The present study was therefore carried out to present an inventory of trace element inputs to agricultural soils in China from all possible sources based on the recently published data. The elements included arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), mercury (Hg), nickel

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(Ni), lead (Pb) and zinc (Zn). The aims were to examine the relative importance of different sources of trace elements, to assess the environmental risks of the trace elements in agricultural land in an effort to provoke scientific attention to this subject and, more importantly, to minimize anthropogenic toxic element inputs in China.

2. Materials and methods

The inputs of trace elements to agricultural soils mainly include atmospheric deposition, livestock manures, fertilizers and agrochemicals, sewage irrigation, sewage sludge, and some other sources such as compost and e-waste. Calculation of element inputs from the sources and environmental risk analysis from these contaminants were described as follows.

2.1. Atmospheric deposition

Total trace element deposition (wet and dry) to agricultural soils was calculated from the average deposition fluxes of each element and the total agricultural land area (1.22×10^8 hectares in 2005) in China. The deposition flux data were collected from the extensive investigation of total deposition in separate regions of China conducted from 1999 to 2006 (e.g. Wong et al., 2003; Tang et al., 2007; Cong et al., 2008). The monitoring sites of the data were selected to be away from industrial or mining pollution sources, mainly located at agricultural land or farms. Although these investigations were not systematic on a national scale, the data from 72 to 178 different sites were supposed to reflect the average level of atmospheric deposition in China. In addition, in order to compare the calculated deposition data, the contribution of selected elements from coal combustion was also estimated as shown in Table S1 in Supplementary Information (SI).

2.2. Livestock manures

Total trace elements in livestock manures were estimated from the livestock numbers raised annually (NBSC, 2006), excretion parameter (Table S2 in SI), and mean element concentrations in each livestock class manures (pigs, cattle, poultry and sheep) based on the survey of total 188 samples collected from 18 provinces or municipalities in China by Liu et al. (2005) and Zhang et al. (2005). Therefore, the trace element inputs to agricultural land from livestock manure were calculated as follows (Nicholson et al., 2003):

$$A_i = f \sum_j N_j P_j (1 - f_{Wj}) C_{ij} \quad (1)$$

where A_i is the amount of trace element (i) input from livestock manures; f is the applied ratio of livestock manures; N_j is the total number of animal (j) raised annually; P_j (kg fresh weight per year) is the excretion parameter of animal (j) (Table S2 in SI); f_{Wj} is the water content in animal (j) manures; and C_{ij} is the concentration of element (i) in animal (j) manures (dry weight). Where all of poultry was treated as chicken since the concentrations of trace elements in other poultry manures were not available, and the concentrations of elements in horse, mule and donkey manures were also substituted by those in cattle manures. Trace element loading rates were estimated assuming the agricultural usage ratio of livestock manures to be 30% according to the investigation of Huang et al. (2006). The nutrients (N, P, and K) contained were also estimated according to the concentration of nutrients in the manures according to the data reported by Xing and Li (1999).

2.3. Fertilizers and agrochemicals

Trace element inputs to agricultural land from fertilizers were estimated from the annual amounts of fertilizer applied (NBSC, 2006) and the contents of trace elements in the inorganic and organic fertilizers (Lu et al., 1992; Wang and Ma, 2004; Liu et al., 2007) as follows:

$$A_i = \sum_j N_j C_{ij} \quad (2)$$

where A_i is the amount of trace element (i) input from fertilizer (j); N_j is the amount of fertilizer (j) actually applied; C_{ij} is the concentration of element (i) in fertilizer (j).

The amounts of Cu and Zn inputs to agricultural land from pesticides were estimated from the forecast of pesticide market of China in 2005 (Wu, 2005).

2.4. Sewage irrigation and sewage sludge

The amount of trace elements released from wastewater (including urban and industrial sources) and the percentage of irrigation water used from wastewater in China were derived from the published data of State Environmental Protection Administration of China (SEPAC) (2006a) and Wang and Lin (2003). The inputs of trace elements to agricultural soils from non-contaminated fresh water were not considered in this study because the concentrations of trace elements in non-contaminated fresh water were extremely low, usually at or below μg/L levels, and that the trace elements accumulated less in soils by irrigation using the fresh water (He et al., 2005).

The quantities of sewage sludge (including urban and industrial sources) produced and released were also based on the data of SEPAC (2006a). Total element inputs to land from this source were estimated from the average concentrations of sludge from 60 cities of China (Chen et al., 2003) and the total quantity of sludge dry solids applied to agricultural land (Mo et al., 2001).

2.5. Others

Except for the above items, various wastes were also identified as being of local importance. However, the industrial wastes are prohibited for land application, and the municipal solid wastes are also mainly treated as landfill or incineration due to their potential hazards from pathogens and toxic pollutants (Wei et al., 2000; SEPAC, 2006a,b; Duan et al., 2008). There are some wastes, such as the wastes from paper mill, food industries and some municipal solid wastes (about 4%), used partially as organic fertilizers after composting (Duan et al., 2008), which had been included in fertilizers. Therefore, these wastes were not considered solely in the inventory. Although there were about 0.6×10^9 tons of crop straw residues for composting (Huang et al., 2006), the contribution of crop straw residues to trace element inputs was also not considered in this study since they come from cropland and most of them would go back to cropland in various ways.

E-waste, as a new emerging point source of trace elements in some local areas, received much attention in China recently (Wong et al., 2007). Over one million tons of e-waste from industrialized countries is flooding into China every year (Qiu et al., 2004). E-waste comprises 3% of pollutants (Wildmer et al., 2005). The disposal of the e-waste was often carried out by primitive methods, such as open burning and strong acid leaching, lacking emission control measures (Wong et al., 2007). The savage disposal has resulted in severe pollution of soils by trace elements as well as polyhalogenated pollutants, which may also affect the surrounding environment by atmospheric movement and deposition (Qiu et al., 2004; Wong et al., 2007). In addition, scattered contamination from abandoned domestic electronic equipments, such as batteries and fluorescent lamps, was also astonishing. For example, the potential amount of Hg released into the environment from wasted batteries reached to 801 tons in 1999 (Yang et al., 2003). However, e-waste was still mainly limited to some specific sites and its contribution to toxic element inputs to agricultural land was of minor importance. Even if any, its contribution to atmospheric pollution has been already considered in atmospheric deposition. Therefore, the actual data were not included in the paper.

2.6. Total net inputs calculation

The total inputs of trace elements annually to agricultural land were estimated based on the items described above. To calculate the net inputs of elements, the outputs from crops were subtracted from the total inputs, and the outputs were estimated as follows:

$$O_i = \sum_j N_j C_{ij} \quad (3)$$

where O_i is the outputs of trace element (i) from crop (j) removal; N_j is the amount of crop (j) produced annually (crop residues were not included) (NBSC, 2006); and C_{ij} is the concentration of trace element (i) in the crop (j) (Wang et al., 2003). It is necessary to note that leaching of trace elements, as an important way to output, was not considered in the mass balance approach since leaching losses are usually relatively small compared to the total quantities entering the soils (Keller and Schulin, 2003; Nicholson et al., 2003). Statistical analysis of the results was performed in SPSS (version 10.0, SPSS Inc.) using ANOVA (Tukey test, $p < 0.05$).

3. Results and discussion

3.1. Atmospheric deposition

Average fluxes of trace element deposition in China as well as their possible variability as the relative standard deviations are provided in Table 1. It is obvious that the deposition fluxes from atmosphere in China were generally higher than those in New Zealand except for Zn and comparable to the highly anthropogenic activities-affected area of Tokyo Bay. According to SEPAC (2006a), the most important sources of trace elements in atmosphere mainly included electric power, nonmetal minerals related plants, black metal smelters, and chemical plants, which accounted for about 77% and 83% of industrial soot and dust, respectively. With the rapid industrialization progress, high temperature industrial processes became a predominant source of trace element aerosols in atmosphere. Actually, most of the industries mentioned above are closely related to coal combustion. About 67% of China's energy needs come from coal combustion and this reliance is not expected to change over the next several decades. According to the amounts of selected elements (As, Cd, Hg and Pb) released to atmosphere during coal combustion (Table S1 in SI), it can be concluded that the released amounts of the elements from coal combustion were comparable to that of calculated from deposition fluxes. For example, the released amount of Hg from coal combustion was well in line with the data of 202 tons in 1999 estimated by Streets et al. (2005) since the consumption of coal in China is increasing significantly. However, not all the emitted elements from coal combustion will go into agricultural land. Most of the elements, even for the volatile ones, would precipitate 20% or more as dry or wet deposition in the proximity of the emission sources. There were still other sources for element inputs from deposition to agricultural land. For instance, Streets et al. (2005) have pointed out that, among the Hg emissions in China, approximately 38% of Hg come from coal combustion, 45% from non-ferrous metal smelting, and 17% from miscellaneous activities, of which battery and fluorescent lamp production and cement production are the largest.

Zinc was the element deposited on soils in the largest amounts from the atmosphere in China, followed by Pb and Cu (Table 1). Zinc and relevant metal mining were also a main source of Hg, Pb and Zn deposition in the atmosphere (Streets et al., 2005). Although Pb-containing gasoline has been prohibited in China since 2002, lead, as the mainly accompanying element of Zn in mining, was consequently higher in the atmosphere deposition (Table 1).

It is noteworthy that the average deposition flux of As in China is about 100 times higher than that in Europe (Nicholson et al., 2003). The average concentration of As in Chinese coal (6.4 mg/kg) is higher than that of the world average (5.0 mg/kg) (Wang et al., 2006). Furthermore, only about 20% of the coal consumed in China were subjected to cleaning (Wang et al., 2006), and most of coal occurred with scattered combustion, lacking necessary emission reduction technologies (Wong et al., 2006). Arsenic is an easily volatile element and prone to be transported for a long range. Therefore, the contribution of coal combustion to As deposition was overwhelming and consistent (Table S1 in SI).

3.2. Livestock manures

Trace elements are presented in livestock diets at background concentrations and may be added as feed additives for health and welfare reasons. For example, As has been used as feed additive for swine and poultry diseases control and weight improvement (Li and Chen, 2005). Although As as an animal feed additive has been abandoned in Europe, it is still in use in some countries such as the USA and China (Li and Chen, 2005). The contents of the trace

Table 1
Trace element deposition fluxes (mg/m^2/yr) in China[a] and other districts.

Element	Number of samples	Range	Mean	RSD[b]	New Zealand[c]	Tokyo Bay[d]
As	76	0.04–11.7	2.8	51%	–	2.9
Cd	118	0.04–2.5	0.40	142%	0.02	0.39
Cr	72	1.11–17.8	6.1	47%	2.8	6.2
Cu	148	0.23–40.9	10.8	67%	3.5	16
Hg	80	0.02–0.50	0.14	106%	–	0.04
Ni	76	0.63–13.8	5.8	47%	0.95	6.8
Pb	148	0.51–75.6	20.2	93%	2.3	9.9
Zn	148	2.91–148.4	64.7	74%	103	–

[a] The data were conducted during 1999–2006.
[b] Relative standard deviation.
[c] During 1999–2001 (Gray et al., 2003).
[d] During 2004–2005 (Sakata et al., 2008).

elements in animal manures consequently increased with the usage of the feed additives.

Typical concentrations of trace elements in livestock manures in China in 2003 are shown in Table 2. The corresponding data monitored in the early 1990s are also provided in Table 2. About 61%, 46% and 42% of the chicken and pig samples exceed the limits for Cd (1.5 mg/kg), Cu (100 mg/kg) and Zn (400 mg/kg), respectively, in reference to the limits of manure compost in Germany (Verdonck and Szmidt, 1998) since no available standards for trace elements in organic manures in China. Exceeding the limits also occurred for other elements in the samples to varying extents. The highest concentrations of Cu and Zn were in pig and chicken manures, with the maximum of Cu and Zn being 1742 and 2287 mg/kg, respectively, reflecting obviously abusive additives in feeds (Liu et al., 2005). Similar trend also existed in cattle manures, although the concentrations of Cu and Zn in cattle manures were not as high as those in pig and chicken manures. The lowest concentrations of Cu and Zn were observed in sheep manures. Arsenic concentrations in chicken and pig manures were also remarkably high compared with those in cattle and sheep manures. Li and Chen (2005) observed that the As concentration in Beijing pig manures, with a mean value of 19.2 mg/kg, was still higher than that in China as a whole, reflecting the higher demand for livestock products in the developed cities in China (Zhang et al., 2005). In addition, the concentration of Cd in the manures was also exceptionally higher than that in the livestock manures of England and Wales (Nicholson et al., 1999), which probably results from the application of phosphorus- or Zn-containing additives.

The concentrations of elements in the manures have been significantly increased from the early 1990s to 2003 although considerable standard deviations occurred for the data (Table 2). In the early 1990s, As concentration in pig manures in China was close to that in England and Wales (Nicholson et al., 1999). However, As concentrations in chicken and pig manures in China have both increased about 10 times over last decade. Similar increment was observed in the Cu and Zn concentrations in chicken and pig manures, although the increment was relative low.

There was about 2.2×10^9 tons of livestock manures produced in China in 2005, with a total nutrient amount of about 23.2×10^6 tons, of which N, P and K accounting for 12.1, 4.4 and 6.7×10^6 tons, respectively. The nutrients contained in the manures were equal to approximately 54%, 60%, and 143% of N, P and K, respectively, from chemical fertilizers applied in 2005. Therefore, the livestock manures were an important resource for agricultural production. However, the predominantly higher concentrations of toxic elements in the manures will pose a potential environmental risk to agricultural production in China if they were excessively applied to croplands in long term (Huang and Jin, 2008). More and more scientists came to recognize the hazards of the toxic elements in the animal feeds and strongly suggested a ban on its use in animal production (Li and Chen, 2005). Due to their potential hazards and accumulated characteristic in agricultural land, the livestock manures must be used with great caution for direct and indirect (mainly used for compound fertilizer) agricultural application before much strict standards for animal feeds are implemented in China.

3.3. Fertilizers and agrochemicals

Trace metal inputs to agricultural soils via fertilizers are of concern due to their potential risk to environmental health. The phosphate fertilizers are generally the major source of trace metals among all inorganic fertilizers, and much attention has also been paid to the concentration of Cd in phosphate fertilizers (Lu et al., 1992; McLaughlin et al., 1996; Nziguheba and Smolders, 2008). However, the environmental hazards of Cd resulted from domestic phosphate fertilizers were not as serious as expected (Table 3). The concentration of Cd in both phosphate rocks and phosphate fertilizers from China was in general much lower than those from the USA and European countries (Table S3 in SI). The concentrations of other elements were also controlled below the national standards for organic–inorganic compound fertilizers (AQSIQ, 2002) and hence safe for use. In addition, trace elements in nitrogen and potassium fertilizers were also safe to agricultural land according to the national standards (AQSIQ, 2002).

Apart from the inorganic or mineral fertilizers, China consumes a significant amount of compound fertilizers annually, reaching about 1.2×10^7 tons (in net nutrients) in 2005 (NBSC, 2006). Compound fertilizers, containing at least two kinds of the three nutrients (N, P, and K), mainly include inorganic compound fertilizers and organic–inorganic compound fertilizers. The organic components of compound fertilizers were miscellaneous, of which livestock manures, sewage sludge (discussed later) and composts from food industrial and municipal solid wastes were often adopted. Therefore the contents of trace elements in the compound fertilizers were remarkably high, especially for Hg and Cd (Table 3). At the same time, China imports a large amount of high quality fertilizers annually including compound fertilizers. For example, about 1.8×10^6 tons of diammonium phosphate (DAP) and 2.3×10^6 tons of NPK compound fertilizers were imported in 2005 (NBSC, 2006). The concentrations of trace elements, especially Cd and Cr in the imported fertilizers containing phosphorus, were significantly higher than those of the domestic fertilizers. It was reported that about 28% of the imported DAP exceeded the national standards for organic–inorganic compound fertilizer for Cd concentration (AQSIQ, 2002) according to a survey of 130 samples of imported DAP (Liu et al., 2007). The application of the imported fertilizers containing phosphorus should therefore be treated with great caution for environmental health reasons.

Table 2
Concentrations of trace elements in selected livestock manures (mg/kg dry weight) in different periods in China (standard deviations were provided in parenthesis).

Element	Chicken manure		Pig manure		Cattle manure		Sheep manure	
	2003 ($n = 70$)	1990s ($n \geq 22$)	2003 ($n = 61$)	1990s ($n \geq 33$)	2003 ($n = 42$)	1990s ($n \geq 66$)	2003 ($n = 15$)	1990s ($n \geq 24$)
As	3.8 (2.1)	0.3 (–[a])	12.8 (5.0)	1.1 (–)	2.0 (2.6)	1.0 (–)	1.5 (1.6)	1.6 (–)
Cd	3.4 (4.3)	0.52 (0.28)	4.8 (7.6)	0.86 (0.98)	3.4 (8.2)	1.4 (1.3)	1.3 (1.3)	2.5 (2.3)
Cr	46.0 (153.9)	20.5 (12.8)	46.6 (62.1)	10.6 (7.0)	15.2 (21.4)	6.1 (5.9)	8.0 (4.8)	11.3 (8.0)
Cu	102.0 (108.3)	52.4 (58.9)	472.6 (310.5)	37.6 (38.9)	46.5 (69.4)	26.9 (23.2)	28.7 (13.2)	44.3 (31.6)
Hg	0.13 (0.10)	0.03 (–)	0.12 (0.23)	0.07 (–)	0.10 (0.10)	0.04 (–)	0.19 (0.50)	0.07 (–)
Ni	15.9 (6.6)	19.5 (11.1)	12.5 (7.2)	12.7 (10.9)	14.1 (6.8)	8.1 (6.6)	12.4 (6.6)	12.4 (6.7)
Pb	20.6 (21.9)	29.3 (49.7)	10.1 (10.9)	13.2 (14.7)	15.7 (11.3)	12.0 (11.7)	12.4 (6.6)	25.8 (41.9)
Zn	308.9 (189.3)	159.6 (101.3)	843.3 (504.2)	137.2 (81.2)	151.9 (125.7)	100.3 (49.8)	123.4 (113.3)	110.5 (60.2)

Sources: Xing and Li (1999), Liu et al. (2005), and Zhang et al. (2005).
[a] No standard deviation is available.

Table 3
Average concentrations of trace elements (mg/kg) in different kinds of fertilizers in China.

Fertilizer	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn
Nitrogen	–	–	–	0.41	0.09	–	0.01	4.9
Potash	–	0.05	–	3.2	0.21	–	–	9.6
Phosphate	15.8	1.2	85.7	44.4	0.88	11.4	38.3	132.7
Compound[a]	17.8	3.0	59.9	61.0	2.1	9.6	27.8	165.4

Sources: Lu et al. (1992), Wang and Ma (2004), and Liu et al. (2007).
[a] Compound fertilizers (which contain at least two kinds of N, P, and K nutrients) include inorganic compound fertilizers and organic–inorganic compound fertilizers.

It is necessary to point out that although the contents of toxic elements in most of the fertilizers in China are lower than the legal limits (AQSIQ, 2002), the trace element inputs to agricultural land were considerable as shown in Table 4 since the annual consumption of fertilizers amounted to 22.2, 7.4 and 4.7 $\times$ 10^6 tons for N, P and K fertilizers (in pure nutrient), respectively (NBSC, 2006). In addition, the amount of fertilizers applied per hectare in China was far higher than that of world average, and the long-term use of excessive nitrogen and phosphate fertilizers has caused serious water eutrophication in some areas and becomes an important non-point pollution source for agricultural land (Lu et al., 2005).

The agricultural use of Hg-, As- and Pb-containing pesticides has been totally prohibited in China since 2002, and only a small number of approved pesticides contain other trace elements, of which Cu and Zn were the extensively used elements for pesticides in China. Copper is mainly used as $CuSO_4$ as a fungicide for fruits, while Zn is a minor constituent of some fungicides, such as mancozeb, that are applied to crops and vegetables. A total input of 5000 tons of Cu and 1200 tons of Zn was estimated to be applied as agrochemical products to agricultural land in China annually (Wu, 2005).

3.4. Sewage irrigation and sewage sludge

The amount of wastewater released has reached 5.25 $\times$ 10^{10} tons in 2005, of which industrial wastewater accounted for 2.43 $\times$ 10^{10} tons (SEPAC, 2006a). Due to the shortage of water resources, wastewater was often used for agricultural irrigation, especially in Northern China. With the implement of environmental regulations on industrial practices and the increase in the ratio of sewage disposal in China, the contents of trace elements in wastewater have been significantly decreased recently (Chen et al., 2003). Consequently, the amounts of most trace elements released have also being decreased over time in the last decade (Table S4 in SI). The estimated inputs of trace elements from sewage irrigation were listed in Table 4 according to the ratio of the sewage irrigating area to the total irrigating area in China (6.6%) and the total amount of water required for irrigation annually (Wang and Lin, 2003; SEPAC, 2006a; NBSC, 2006).

Similar to wastewater, the concentrations of trace elements in sewage sludge have also been markedly reduced, and most of them were below the national discharge standard of pollutants for municipal wastewater treatment plants (Table S5 in SI). However, due to the huge increase in the amount of wastewater treated, the sewage sludge produced increase rapidly. Approximately 4.6 $\times$ 10^6 tons (dry weight) of municipal sewage sludge was produced in China in 2005 (SEPAC, 2006a). Although land application was considered as one of the most cost-effective options of sludge disposal, the application of sewage sludge to agricultural land was very low (below 10%) due to the toxic substances in it (Mo et al., 2001). The inputs of trace elements from direct sewage sludge application were estimated as shown in Table 4 assuming that the ratio of direct agricultural land application was 10%. Sewage sludge could also contribute to the total trace element inputs from indirect application, such as used for compound fertilizer production, which has been included in the items of fertilizers as stated above.

3.5. An inventory of trace element inputs

Annual trace element inputs as well as net inputs to agricultural land in China from all the sources considered are compiled in Table 4. For As, Hg, Pb, and Ni, 58–85% of the total annual inputs to agricultural land were derived from atmospheric deposition, only 8–25% and 5–30% from livestock manures and fertilizers, respectively. In contrast, about 69% and 51% of Cu and Zn inputs, respectively, were from livestock manures. For Cd, 55% of inputs were from livestock manures, 35% from atmospheric deposition, and only 8% from fertilizers (mainly compound fertilizers). The main sources of Cr were atmospheric deposition (43%), livestock manures (36%) and fertilizers (20%).

3.6. Environmental risk analysis and management

The current increasing rates of trace elements in soils were used to estimate the time (years) required to raise the concentrations of trace elements in topsoil (0–20 cm) from background values (Chen et al., 1991) to the limits regulated by the environmental standards for trace metals in agricultural soils (SEPAC, 2006b). After approximately 400 years, if at present rates, the concentrations of Cu and Zn in soils would exceed their limits, i.e., 100 mg/kg for Cu and 250 mg/kg for Zn, respectively. It is particularly concerned that the

Table 4
Annual trace element inputs (tons) to agricultural soils in China.

Source	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn
Atmospheric deposition	3451	493	7392	13,145	174	7092	24,658	78,973
Livestock manures	1412	778	6113	49,229	23	2643	2594	95,668
Total fertilizers	835	113	3429	2741	87	504	1565	7874
Nitrogen + Potash	nd	0.61	nd	62	7.8	nd	0.67	389
Phosphate	299	24	1626	843	17	215	727	2518
Compound	536	89	1803	1836	62	289	838	4967
Agrochemicals	0	<1	<1	5000	0	0	0	125
Irrigation water	219	30	51	1486	1.3	237	183	4432
Sewage sludge	7.4	1.4	85	224	1.3	36	60	669
Total input	5925	1417	17,071	71,824	286	10,512	29,061	18,7741
Total output	192	178	1038	12,158	18.2	2432	208	60,792
Net input	5733	1239	16,033	59,666	268	8080	28,853	126,949
Increment (mg/kg/yr)[a]	0.02	0.004	0.057	0.21	0.001	0.029	0.10	0.45
Time required (yr)[b]	920	50	2433	364	455	802	525	389

[a] Calculations assume a soil density of 1.15 g/cm^3 and a plough depth of 20 cm.
[b] Time required to raise soil trace element concentrations from background (Chen et al., 1991) to the limit concentrations (SEPAC, 2006b).

input of Cd to agricultural land was so high that exceeded our expectation. It will only take about 50 years for Cd to exceed the current environmental standard (0.3 mg/kg for soil with pH 6.5–7.5) (SEPAC, 2006b) if its input rate remains at the current 0.004 mg/kg/yr. Of course, the result would be less pessimistic if considering the output contribution from leaching. However, these times might be significantly shortened in the areas if element concentrations in soils were already elevated above the background values. Moreover, spatial heterogeneity occurred for the contamination sources, even for atmospheric deposition, which will no doubt accelerate the soil contamination in some areas. If livestock manures or sewage sludge were applied to, for example, 30% of the total agricultural land area referring to their application rates in China, the times to exceed the safe limits would be at least halved for the soils. Therefore, the soils actually exposed to contamination by trace elements were often more severe than estimation, especially in the developed regions. Effective measures must be taken to attenuate the environmental pressure resulted from trace element contamination, and particularly it should chose Cd as the prior monitoring goal when contamination sources were controlled.

It is necessary to note that, as stated above, there will be uncertainty when the nationwide inventory is used on a scale of small or specific regions due to variation in agricultural amendments (livestock manures, sewage sludge, fertilizers, etc.) and spatial and temporal heterogeneity in trace element sources. For example, relatively large variations occurred to the concentrations of trace elements in atmospheric deposition and livestock manures, with standard deviations that were of the same order of magnitude as their average values (Tables 1 and 2). However, as a nationwide inventory, it clearly demonstrated that agricultural soils are potentially at risk of trace element accumulation from direct and indirect application of livestock manures. It is therefore necessary to introduce the allowable limits of livestock manures to agricultural land before more tightened regulations on feeds and feed additives being implemented. Also it is as necessary as the improvement of the regulation to develop the practical technologies for cleaner production in swine and poultry husbandry. In order to control the release of trace elements from coal combustion to atmosphere, the stricter regulations should be implemented on coal washing, which can reduce 30% more of total toxic elements in it (USEPA, 2002). This is especially necessary for residentially burning coal.

4. Conclusions

Inputs of trace elements to agricultural soils via all possible sources were analyzed, and their current status and future prospect were assessed. Atmospheric deposition and livestock manures were the predominant sources of trace elements entering agricultural land. Phosphate fertilizer was not the main source of trace element inputs in China, even for Cd. However, the element inputs from fertilizers, sewage sludge, as well as e-waste, should also be carefully monitored and regulated as they often occurred at excessively higher rates in some areas. According to environmental risk analysis, it is evident that Cd is the element of prior concern for agricultural soils. So that stricter strategies may be needed at a national level to control and reduce toxic element inputs and to preserve long-term quality of agricultural soils.

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Appendix. Supplementary data

Table of the amounts of selected elements released from coal combustion and atmospheric deposition, table of parameters of animal excretion and annual population of different livestock in China, table of Cd content in phosphate rocks and phosphate fertilizers from China and some other countries/districts, table of the annual released amounts of trace elements from wastewater in China, and table of occurrence of trace elements in sewage sludge in China.

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jenvman.2009.01.011.

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