Effects of using wastewater and biosolids as nutrient sources on accumulation and behaviour of trace metals in Vietnamese soils

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Abstract

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This study investigates the impacts of wastewater and biosolids application on cultivated Vietnamese Fluvisols and Acrisols. Chemical impacts, i.e. enrichment of macronutrients (N, P, K) and trace metals (mainly Cu, Zn, Cd, Pb), and solubility and mobility of trace metals were examined. Experiments were carried out in peri-urban vegetable and/or rice-dominated farming systems of Hanoi, Ha Tay, Vinh Phuc and Nam Dinh cities. Batch studies were performed in order to measure metal solubility in soil solution, and multi-surface models including the soil sorption surfaces, i.e. iron hydroxides (DLM), organic matter (SHM and NICA-Donnan model), and phyllosilicate clay (Gaines-Thomas) were tested for describing metal binding. A multi-surface model was used to run various scenarios including (i) changing metal loading (Cd, Cu, Zn) up to the present Vietnamese maximum acceptable soil concentration (MAC), and (ii) varying soil organic matter (SOM) content and (iii) soil pH within the ranges found in the national soil inventory of Acrisols and Fluvisols, respectively. These soil types represent 73% of agricultural soils in Vietnam.

Field balance calculations revealed macronutrient and trace metal (Cu, Zn) accumulation in intensive peri-urban vegetable systems in Hanoi City. The N surplus ranged from 85-882 kg ha^{-1} yr^{-1}, while P and K surpluses were 109-196 and 20-306 kg ha^{-1} yr^{-1}, respectively. For Cu and Zn surpluses varied from 0.2-2.7 and 0.6-7.7 kg ha^{-1} yr^{-1}, respectively, wastewater and biosolids being the major sources accounting for 75-98 and 62-94% of the total Cu and Zn input. Application of biosolids significantly increased the 'total' (reverse *aqua regia*-extractable) soil Zn concentration, whereas concentrations of Cd and Pb were not significantly different from the control. However, there were positive relationships between EDTA-extractable Cd, Cu and Zn and biosolids application rates. For total dissolved Cd, Cu and Zn the multi-surface models provided very good model fits for all soils and thus these can be used to describe their binding and solubility in tropical Fluvisols and Acrisols. Scenario simulations identified the potential risk of metal losses to the environment (i.e. Cd and Zn), as influenced by loading up to MAC, soil acidification and decreasing soil organic matter content, especially for Acrisols. Assuming the same metal input rate as at present, it was roughly estimated to take 20-325 and 40-450 years to reach the MAC for Cu and Zn, respectively. It was concluded that wastewater and biosolids can be major nutrient sources in peri-urban agricultural production systems. However, they can also contribute to substantial trace metal inputs and represent a potential threat to soil quality, water environment and human health. Soil organic matter is a major sorbent for Cd, Cu, and Zn in tropical Acrisols and Fluvisols, and pH is the main factor controlling the solubility of metals in these soils. Regarding Pb, modelling was not successful and further refinements of the models will be required.

Key words: Adsorption, biosolids, cadmium, copper, modelling, trace metal, Vietnam, wastewater, zinc

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Dedicated to Hằng and Quốc

Contents

Appendix

Paper I-IV

This thesis is based on the following papers, which are referred to in the text by their Roman numerals:

I. Khai, N.M., Ha, P.Q. & Öborn, I. 2007. Nutrient flows in small-scale peri-urban vegetable farming systems in Southeast Asia - A case study in Hanoi. *Agriculture, Ecosystems & Environment 122*, 192-202.

II. Khai, N.M., Ha, P.Q., Vinh, N.C., Gustafsson, J.P. & Öborn, I. 2007. Effects of using wastewater and biosolids as nutrient sources on soil chemical properties in peri-urban agricultural systems (*Manuscript*).

III. Khai, N.M., Öborn, I., Hillier, S. & Gustafsson, J.P. 2007. Modelling of metal binding in tropical Fluvisols and Acrisols treated with biosolids and wastewater (*Submitted to Chemosphere*).

IV. Khai, N.M., Öborn, I. & Gustafsson, J.P. 2007. Simulated effects of metal load, soil organic matter and pH on the solubility of Cd, Cu and Zn in Fluvisols and Acrisols in SE Asia (*Manuscript*).

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I am the first author on all papers, and thus primarily responsible for the field and laboratory work, modelling, statistical analysis, data interpretation, illustrations and the text. The co-authors contributed to the field and laboratory work, modelling, data interpretation, method development and discussion.

Photo coverpage: The two photos at the bottom left were taken by Martin Larsson

Introduction

In many countries of south-east (SE) Asia, urbanisation has been progressing rapidly during recent decades (UN, 2002). Inadequate handling of urban waste and high intensity agricultural cultivation in peri-urban areas are having negative effects on the environment (*e.g.* Brook & Davila, 2000; Anh *et al.*, 2004). Urbanisation has always involved an increased one-way transfer of food from countryside to town and thereby also accumulation of plant nutrients in urban waste products (*e.g.* Huang *et al.*, 2006). Many countries are now facing severe pollution problems in rivers, lakes and along coasts because of heavy loads of municipal wastewater and sewage being discharged directly into water bodies. Industrial, agricultural and domestic effluents such as solid wastes and wastewater are either dumped on land or are used for irrigation purposes, which creates both opportunities and problems (*e.g.* Dirkzwager & L'Hermite, 1989; Yadav *et al.*, 2002; Lazarova & Asano, 2005).

Vietnam is an agricultural country. The natural land area is 33.1 million ha, of which agricultural land occupies 9.4 million ha (MONRE, 2007). The population in 2005 was 83.1 million, of whom more than 73% live in rural areas (GSO, 2006). The national gross domestic product (GDP) in 2005 was 175 000 billion VND (16 000 VND ≈ 1 USD), 20% of which came from the agricultural sector (GSO, 2006). Agriculture in Vietnam has made great progress in recent decades. Since 1996, rice export has remained stable at between 3 and 4.5 million tons yr^{-1}. There are 4.2 million ha of agricultural land used for rice cultivation, *i.e.* 44% of the agricultural area, located mainly in the Mekong delta and the Red River delta (MONRE, 2007). In the northern parts of the country, rice is grown in one of the crop rotations rice-rice, rice-rice-corn/beans, or rice-rice-winter vegetables (normally tomato, cucumber and cabbage). In the south, rice is grown predominantly in continuous rice systems with two or three rice crops per year. Soils used for rice cultivation are mainly alluvial soil (Fluvisols) in lowland areas (Cuc, 2003; Nguyen, 2003).

The urbanisation, industrialisation and modernisation of Vietnam are giving rise to increased consumer demand for food products. This places pressure on agriculture, which has to increase agricultural production for domestic consumption as well as for export. Agricultural land use is becoming more intensive, with increasing use of fertilisers and pesticides. This is especially true in peri-urban areas surrounding large cities where rice has often been replaced by cultivation of vegetables, flowers *etc.* for the city market (Richter & Roelcke, 2000; van den Berg, van Wijk & van Hoi, 2003; Hoang Fagerström *et al.*, 2006). However, urbanisation and industrialisation processes also lead to increased production of waste, *i.e.* wastewater and solid waste. Some solid wastes contain high amounts of organic matter and nutrients and are therefore used as organic fertilisers (biosolids). In this thesis the term biosolids refers to solid waste used as an organic fertiliser, including sewage sludge (from municipal wastewater treatment plants or industrial processes), animal manure, crop residues, household compost *etc.* To balance the transfer of nutrients with food from rural to urban areas, these wastes should be recycled back to agricultural systems, but there are side-effects involved and agricultural land is experiencing contamination with potential pollutants such as trace metals. Therefore, there is an urgent need to increase understanding of the effects of reusing wastewater and biosolids for agricultural cultivation in terms of nutritive value and potential risks. Predictive modelling tools combined with experimental data addressing the effect of waste products on trace metal content in soils are necessary for appropriate use of waste on agricultural land and for reducing the risk of negative environmental consequences.

Objectives

The overall objective of this thesis was to improve knowledge of the impacts of reuse of wastewater and biosolids as water and nutrient sources on cultivated tropical Acrisols and Fluvisols in SE Asia. Emphasis was placed on the chemical impact of those applications on the soils, *i.e.* enrichment of macronutrients (N, P, K) and trace metals, and solubility and potential mobility of trace metals (Cd, Cu, Pb and Zn). A combination of field studies, laboratory experiments and chemical modelling was used as a study method. Peri-urban agricultural areas in Vietnam were used as field study sites.

The hypotheses for the thesis work were that:

i) Waste material (wastewater and biosolids) from the city is a major nutrient source in peri-urban agriculture.

ii) Reuse of wastewater and biosolids in agriculture leads to accumulation of trace metals in soils.

iii) Soil pH is the main factor controlling solubility and mobility of trace metals (Cd, Cu, Pb and Zn) in tropical Acrisols and Fluvisols.

iv) It is possible to use multi-surface equilibrium models to describe metal binding in tropical Acrisols and Fluvisols.

v) There is a low risk for trace metal pollution of surface water and groundwater as a result of long-term application of wastewater and biosolids to soils (tropical Acrisols and Fluvisols).

The specific objectives were:

i) To study management-related element fluxes and field balances of nutrients (N, P, K) and trace metals (Cu, Zn) in two small-scale peri-urban agricultural systems upstream and downstream from a large city in SE Asia. The mass balance approach was applied to assess imbalances and soil accumulation rates in case studies at field level in two peri-urban villages within the Hanoi area, Vietnam (*Paper I*).

ii) To quantify the soil chemical effects of (a) biosolids application and (b) long-term wastewater irrigation on general soil characteristics (*i.e.* pH, EC, soil organic matter and total nitrogen) and trace metal accumulation and speciation (main focus on Cd, Cu, Pb and Zn) (*Paper II*).

iii) To investigate whether it is possible to use chemical equilibrium models (multi-surface models) to describe trace metal binding (Cd, Cr, Cu, Mn, Pb and Zn) in some tropical soils (Acrisols and Fluvisols) amended with biosolids and wastewater. Organic complexation models were combined with a surface complexation model for Fe and Al (hydr)oxides and with ion exchange to phyllosilicate clays, and applied to predict trace metals dissolved in the soil solution (batch experiments) *(Paper III).*

iv) To assess the effects of soil organic matter, pH and soil trace metal (Cd, Cu and Zn) concentrations ('total', reverse *aqua regia*-extractable) on the solubility of these metals. A multi-surface model (see iii) was used to test various scenarios for Vietnamese Acrisols and Fluvisols, including the effect of increased metal loads up to the maximum allowable concentration (MAC) *(Paper IV).*

Background

Sources of trace metals in agricultural soils

Trace metals in agricultural soils have both natural and anthropogenic sources (*e.g*. Ross, 1996; Siegel, 2002). Mineral rock is an original source of metals found in soils and aquatic environments and weathering of the rock provides the natural source of metal inputs to soil-plant systems. Since soils are derived from different parent materials, trace metal concentrations can vary widely in different soils (Ross, 1996).

Although all trace metals are released in varying quantities from parent materials into soil, significant amounts of certain metals found in soil are derived from other sources. Figure 1 shows the trace metal cycle in the soil environment. The accumulation of trace metals in agricultural soils is mainly the result of application of mineral and organic (biosolids) fertilisers, use of lime and other soil amendments, wastewater irrigation and atmospheric deposition (*e.g.* van Driel & Smilde, 1990; Ross, 1996; Moolenaar & Lexmond, 1998; Römkens & Salomons, 1998). Topsoil trace metal concentrations are influenced by vegetation recycling and, at best, these elements show very slow movement down the soil profile (Ross, 1996).

Atmospheric deposition is often a significant input of trace metals, especially for certain metals such as Pb and Cd, *e.g.* originating from fossil fuel combustion, metal smelters and other industrial sources (Kelly, Thornton & Simpson, 1996;

Zhang *et al.*, 2002; Wong *et al.*, 2003). Trace metal deposition varies between different regions (Table 1).

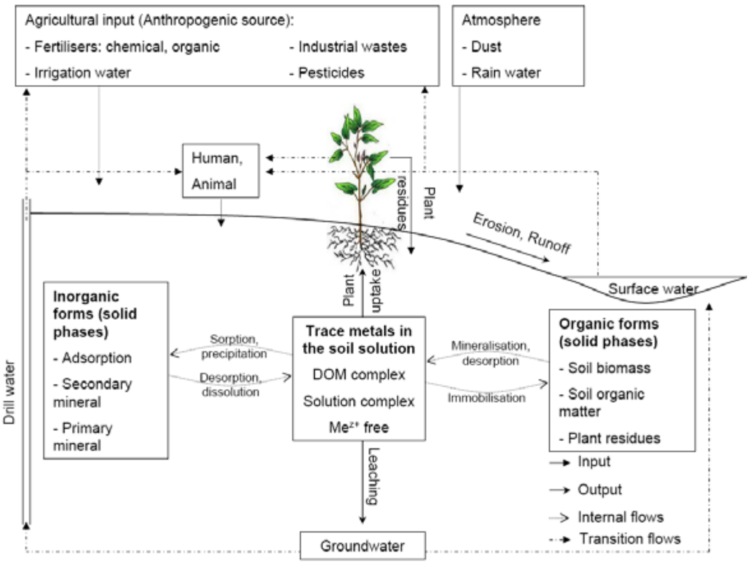

Figure 1. Cycling of trace metals in an agricultural soil system. Me^{z+} free means hydrated metal ions, *i.e.* aqua-complexes such as $Me(H_2O)_x{}^{z+}$ (modified from Brady, 1994; Chapman *et al.*, 2003; Pierzynski, Sims & Vance, 2005).

Chemical and organic fertilisers (biosolids) are commonly used in intensive agriculture (McLaughlin & Singh, 1999), and in tropical agricultural soils in particular, crop production is usually enhanced by application of rather large amounts of fertilisers (Naidu, Sumner & Harter, 1998). However, high concentrations of trace metals have been found in the material of impure fertilisers such as phosphate fertilisers and refuse-derived compost (Pezzarossa *et al.*, 1990; Sikora & Giordano, 1995; McLaughlin *et al.*, 1996; Table 1). Phosphate fertilisers have been significant sources of Cd in soils remote from industrial pollution sources (Page, Bingham & Chang, 1981; McLaughlin *et al.*, 1996; Mortvedt, 1996; McLaughlin & Singh, 1999). Biosolids can contain high concentrations of certain metals, depending on the origin of the material (Mortvedt, 1996; Nicholson *et al.*, 2006). Even if fertiliser applications do not give rise to concentrations high enough to be initially toxic, critical levels can build up as a result of repeated applications (McGrath *et al.*, 1982; Ross, 1996; McLaughlin *et al.*, 2000).

Irrigation water can be another source of trace metals. Reused wastewater is an important source of irrigation water in agricultural production (van der Hoek *et al.*, 2002; Lazarova & Asano, 2005). However, poor irrigation water quality is one of the main factors limiting plant growth and influencing crop quality. Wastewater effluents generally contain high concentrations of suspended and dissolved solids, both organic and inorganic, and these contain trace metals that may be a significant input source of metals for agricultural soils (Haruvy, 1997; Mohammad & Mazahreh, 2003; Lazarova & Asano, 2005).

Table 1. *Some reported data from relevant areas on trace metal amounts/concentrations in atmospheric deposition, biosolids, mineral fertilisers and irrigation water*

Source/Location	Cu	Zn	Cd	Pb	Reference
Atmospheric deposition (mg m^{-2} yr^{-1})					
Bombay, India	17	98	0.6	12	Tripathi, Ashawa & Khandekar (1993)
Amman[a], Jordan	6	30	0.15	4	Momani, Jiries & Jaradat (2000)
PRD[b], China	11-41	58-164	0.01-0.14	2.9-25	Wong *et al.* (2003)
Kanto, Japan			0.08-0.13	1-3	Itoh, Miura & Yoshinaga (2006)
Northern Vietnam[c]	0.001	0.01		0.01	Wagner, Pettersson & Boman (2007)
Northern China	5			5	Han *et al.* (2007)
Biosolids (mg kg^{-1} dw)					
YRD[d], China	23-350	20-422	0.05-0.07	11-22	Huang *et al.* (2006)
TPS[e], Taiwan	547	2030	5.6	59	Hseu (2006)
Vietnam	2-60	15-250	0.3-0.8	7-15	Khoa *et al.* (2005)
Hanoi, Vietnam	48-96	255-359	0.24	0.4	Hoang Fagerström *et al.* (2006)
Chemical fertilisers (mg kg^{-1})					
YRD[d,f], China	0.1-23	12-48		3-10	Huang *et al.* (2006)
Vietnam[f]	1-300	50-1450	0.1-170	7-225	Khoa *et al.* (2005)
Irrigation water (μg L^{-1})					
YRD[d,g], China	1-3	1-33	0.03	0.2	Huang *et al.* (2006)
Hanoi[g], Vietnam	48-131	108-210	0.9-33	40-158	Tra *et al.* (1998)
Hanoi[h], Vietnam	38-807	58-430	0.2-24	7-413	Tra *et al.* (1998)
Hanoi[h], Vietnam	20-850	20-180	n.d.	20	Hoang Fagerström *et al.* (2006)

n.d. = Not detected (below detection limit); [a]Dry deposition; [b]Pearl River Delta region, China; [c]Estimated in fine particle fraction ($PM_{2.5}$); [d]Yangtze River Delta region; [e]Sewage treatment plant for Kaohsiung City in southern Taiwan; [f]Phosphate fertilisers; [g]River water; [h]Wastewater from Hanoi city.

Reuse of biosolids in agriculture

Agricultural use of biosolids as fertilisers is a disposal method used in many countries. The application of organic waste in the form of sewage sludge to agricultural land began in the 1920s and is increasing in many parts of the world (Oliver, McLaughlin & Merrington, 2005). Nearly half of the sewage sludge production in the United States is currently being applied to land. In the European Community, over 30% of the sewage sludge produced is used as a fertiliser in agriculture (Silveira, Alleoni & Guilherme, 2003). Currently approximately 0.25 million tonnes (dry weight) of sewage sludge are produced annually in Australia, with perhaps one-third to half of this being applied to land (Molloy *et al.*, 2005). However, health and environmental risks due to occurrence of contaminants *i.e.*

heavy metals, organic compounds, pharmaceutical residues *etc.*, have severely limited recycling of sewage sludge to arable land in several countries (*e.g.* Sweden, the Netherlands) (Veeken, 1998; EU, 2001; Bengtsson & Tillman, 2004). Biosolids in the form of animal manure, such as poultry, cattle and pig manure can be used directly as organic fertilisers for agricultural purposes. They can also be mixed with crop residues or household waste to increase the nutrient value of the composted manure as a soil additive (Molloy *et al.*, 2005). In addition to nutrients, animal manure may contain high concentrations of certain metals used as feed additives (Alloway, 1995). Pig and poultry manures contain elevated concentrations of Cu and Zn, which are fed to improve food conversion efficiency, while in certain countries As is also used for this purpose (Rosal, Momplaisir & Heithmar, 2005). Nicholson *et al.* (1999) reported the average Cu concentration in pig manure in England and Wales to be 360 mg kg^{-1} dry weight (dw) and the Zn content 500 mg kg^{-1} dw, while trace metal concentrations in poultry manure were 80 mg Cu kg^{-1} dw and 400 mg Zn kg^{-1} dw.

Application of biosolids to agricultural land appears to be a logical and reasonable use of these waste products, since it may improve many soil properties, such as pH and organic matter and nutrient content, as well as soil physical properties (Karapanagiotis, Sterritt & Lester, 1991; Tsadilas *et al.*, 1995; Sastre, Vicente & Lobo, 2001; Horswell, Speir & van Schaik, 2003). Concerning the wider environmental prospects, the use of biosolids for agriculture gives benefits such as conservation of the environment, reduced costs for fertiliser inputs and disposal of the waste in a low-cost and hygienic way (SAEPA, 1996). However, potentially toxic trace metals in biosolids applied to land will accumulate in the soil, or risk being transported to surface waters and groundwater (*e.g.* Ross, 1996; McLaughlin *et al.*, 2000; Vaca-Paulin *et al.*, 2006; Chaudri *et al.*, 2007).

In Vietnam, the biosolids used as fertilisers on agricultural land are mainly in the form of farmyard manure (FYM) (NISF, 2003). About 65-70 million tons of FYM are produced annually in Vietnam from pigs, livestock and poultry (VEPA, 2005). It is estimated that two-thirds of this FYM is used for rice and vegetables, and the rest is applied to other crops such as coffee, tea, peppers, strawberries, *etc*. In addition, in rural areas where households do not have septic tank systems, composted human faeces are normally used for crops, particularly for vegetables and flowers. For example, in five peri-urban districts surrounding Hanoi City, 34-40 thousand tons of human faeces are applied annually to vegetable crops (Khoa *et al.*, 2005). In the past, many local farmers used fresh manure, but this practice could cause a direct risk to human health since it could be a route for disease transmission. Nowadays, farmers are changing from using fresh manure to using composted mature manure. Biosolids are mainly stored and incubated before application to the field and the abundance of harmful pathogens such as helminths, bacteria and viruses decreases during incubation (NISF, 2003).

Reuse of wastewater in agriculture

Reusing wastewater for irrigation in agricultural cultivation is common practice in many countries, especially in many arid and semi-arid regions (Lazarova & Asano, 2005). The advantages of reusing wastewater are that it provides convenient disposal of discharge water and has the beneficial aspects of adding valuable plant nutrients and organic matter to soil. Even in areas where wastewater is not the sole water source for agricultural irrigation, farmers still prefer using sewage for irrigation by reason of its nutritive value, which reduces expenditure on mineral fertilisers (*e.g.* Pescod, 1992; Lazarova & Asano, 2005). However, irrigation water quality is one of the main factors limiting plant growth and influencing crop quality (AlNakshabandi *et al.*, 1997; Barman *et al.*, 2001; Muchuweti *et al.*, 2006). The trace metal content of suspended and dissolved solids in wastewater may also affect the soil biota and the external environment (*e.g.* Haruvy, 1997; Mohammad & Mazahreh, 2003; Lazarova & Asano, 2005).

In Vietnam, a nationwide survey in 54 provinces/cities in 2001 found that 75% of domestic wastewater in large cities and 45% in smaller cities is discharged into sewers. Wastewater was used for agriculture or aquaculture in 93% of Vietnamese cities. However, the area of agricultural land irrigated by wastewater only accounted for 2% of the total area around most cities, and was predominantly used for growing rice (Raschid-Sally, Tuan & Sarath, 2004) but also used for aquatic vegetables and aquaculture (Anh *et al.*, 2004; Hoan & Edwards, 2005; Hoang Fagerström *et al.*, 2006). The total area irrigated with wastewater was conservatively estimated at around 9000 ha (Raschid-Sally, Tuan & Sarath, 2004). Most cities in Vietnam have some sewerage and wastewater drainage coverage. Sewerage systems are covered networks but the drains carrying city wastewater may be open. In many cities, industrial wastewater is sometimes discharged into municipal collection systems when an alternative is not available (Anh, Barreiro & Parkinson, 2005). Industries close to rivers tend to discharge their wastewater directly into these rivers (Raschid-Sally, Tuan & Sarath, 2004).

Factors affecting solubility and binding of trace metals in soils

Sorption of trace metal ions on soil constituents is influenced by a variety of factors, the most important being pH, redox conditions, type and speciation of the metal ion concerned, trace metal competition for sorption sites, soil composition and ageing.

Soil pH

Soil pH is the main factor controlling the solubility and availability of trace metals in soils of varying texture, soil mineralogy and organic matter content (*e.g.* McBride, 1994). Trace metal cations are most soluble and available under acidic conditions. Soil solution extracts from field and pot experiments from a range of soil types maintained at different pH conditions have shown that Cd, Cu, Pb and

Zn are much more soluble at pH 4-5 than in the pH range 5-7 (*e.g.* Brummer & Herms, 1983). Inventories of Vietnamese soils including 231 Acrisols and 206 Fluvisols made by Ha *et al.* (2003; 2005) showed that 51% and 21% of the soils, respectively, had pH values within the range 4-5. Christensen (1984) found an approximately threefold linear increase in Cd sorption capacity for each pH unit increase within the range pH 4.4-7. Kerndorf & Schnitzer (1980) found 50% of Cd or Zn to be absorbed onto soil humic acid at pH values between 4.8-4.9, while the pH for Cu was lower. Naidu, Sumner & Harter (1998) reviewed sorption of trace metals in variable-charge tropical soils and concluded that trace metals in the soil solution could be markedly reduced by increasing soil pH via liming or other strategies. Cadmium sorption in three tropical soils (Oxisol, Ultisol, Mollisol) displays a greater pH dependence than Pb (Appel & Ma, 2002). At pH values above 7, the solubility of metals may increase due to binding with dissolved organic matter (DOM), since the solubility of solid soil organic matter (SOM) increases with increasing pH (You, Yin & Allen, 1999).

Soil pH also affects precipitation of metals, *e.g.* the hydroxide form. Under alkaline conditions (pH>7.0) and at very high Cd^{2+} activities, precipitation of Cd may occur. A study on adsorption of metals on titanium oxides showed that Cu and Mn adsorption and precipitation were pH-related. At pH<6, adsorption predominated while at pH>6, precipitation predominated (Bleam & McBride, 1986). A similar pattern has been reported for Pb (Harter, 1979; Barrow, 1986).

Redox conditions

Redox potential (Eh) is one of the critical factors regulating the speciation and bioavailability of metals in soils. Theoretical predictions have been made of trace metal equilibria as affected by pH and redox potential (Kabata-Pendias & Pendias, 2001). Oxidation-reduction reactions may affect not only the partitioning of redox-active trace metals such as Cr, Mn or Mo, but also that of redox-stable metals such as Cu, Ni or Zn in the soil environment (McBride, 1994). In natural soil conditions, pH most often ranges between 5 and 7, while Eh ranges between 400 and -200 mV, except where there are highly reducing conditions in waterlogged soils (Kabata-Pendias & Pendias, 2001). Most often, the mobility of trace metals, especially of Cd, Cr and Zn, increases in poorly aerated soils (Ross, 1996). However, increasing Cd solubility with increasing Eh up to >200 mV has also been observed (Morel, 1997).

The most characteristic difference between paddy soils and upland soils is a drastic shift in the oxidation-reduction state. The redox potential of the soil often decreases to -100 mV or even lower within a month of flooding (Iimura, 1981; Patra & Mohanty, 1994; Kashem & Singh, 2001) and is lower for soils treated with organic matter compared with untreated soils (Kashem & Singh, 2001). Upon submergence, the availability of metals in soils is reported to decrease, an effect attributable to increased adsorption of metal on hydrous Mn and Fe oxides (Brown *et al.*, 1989) and formation of insoluble compounds with sulphide (*e.g.* CdS, ZnS, PbS) (Iimura, 1981; Chaney *et al.*, 1996; Kadlec & Knight, 1996; van den Berg, Loch & Winkels, 1998). In addition, flooding causes increased pH and consequently decreases solubility (Patra & Mohanty, 1994; Narteh & Sahrawat, 1999; Tinh, 1999; Kashem & Singh, 2001). Cultivated rice soils in Vietnam are generally switched from flooded to non-flooded conditions, *e.g.* at the critical grain filling stage, in order to optimise yields and facilitate ease of harvesting, and that decreases soil pH and increases trace metal phytoavailability. In addition, increased acidity upon drainage and oxidation also results in the dissolution of secondary Al precipitates and the release of any sorbed trace metals (Simmons *et al.*, 2005), especially under severely acidic conditions as in acid sulphate soils (Tinh, 1999).

Complex hydroxide chemistry processes can lead to precipitation. Dissolved OH^-, HCO_3^-, and CO_3^{2-} ions can form precipitates with trace metals, for example as $CdCO_3$ and $Co(OH)_2$. Conversely, oxidation also results in the formation of Fe and Mn oxides and some subsequent sorption of trace metals (McBride, 1994).

Organic matter

Soil organic matter (SOM) consists of a mixture of plant and animal products in various stages of decomposition and to various extents, and also of humic substances believed to be synthesised either chemically or biologically. This complex material is traditionally divided into humic and non-humic substances. Organic matter is widely distributed in soils and has been identified as playing an important role in controlling solubility and mobility of trace metals in soil systems (Brown & Parks, 2001; Kretzchmar & Voegelin, 2001; Weng, Temminghoff & van Riemsdijk, 2001; Gustafsson, Pechova & Berggren, 2003).

The most stable compounds in soils are humic substances (HS) operationally partitioned into the fractions humic acid (HA), fulvic acid (FA) and humin, which are similar in structure but differ in their reactions and molecular weight (McBride, 1994). In many cases, the stability of metal complexes with FA and HA acids increases with increasing pH from 3 to 7. Fulvic acids have a higher concentration of reactive groups, dissociating at $pH<7$ compared with HA (Tipping, 2002), and therefore they exhibit a higher capacity to form stable complexes with metal ions compared with HA. The FA fraction of dissolved organic matter (DOM) has been found to be a major constituent of the natural ligands complexing Cu in the case of stream water with relatively high Cu concentrations and low pH (Breault *et al.*, 1996). Hanbin & Laura (1999) reported a much higher concentration of Cu and Cd in FA compared with HA.

The competitive sorption of protons, trace metal cations and major cations to natural organic matter from soils has been discussed by many authors. Kinniburgh *et al.* (1996) reported that the presence of Cd significantly reduced Ca binding to a purified peat HA. On the other hand, Cd binding was decreased by increasing Ca concentrations in the HA suspensions. A study by Pinheiro, Mota & Benedetti (1999) showed sorption competition between Ca and Pb to a Podsol FA in Canada and observed a clear reduction in Ca binding in the presence of Pb.

Dissolved organic matter may control the behaviour of metals in the soil solution in most situations, since the majority of dissolved metals are often found in metal-organic complexes (Sauvé *et al.*, 1997). In addition, when most of the metals in solution are bound to DOM, any factor that influences organic matter solubility also affects metal solubility (Fotovat & Naidu, 1998; Römkens & Dolfing, 1998; Sauvé, Hendershot & Allen, 2000). The application of domestic wastewater to agricultural soil has been found to increase the short-term solubility of trace metals due to increasing DOM in the soil solution. Brummer & Herms (1983) reported that at pH values below 6, the concentration of Cd was much lower in the equilibrium solution of soils with higher total organic matter content. Therefore, soil organic matter can reduce the toxic effects of Cd in contaminated soil in acidic conditions. In contrast, at pH 6-8, higher Cd concentrations have been measured for soil samples with higher organic matter content because of complexation of Cd by DOM (Brummer & Herms, 1983). A study in rice fields by Kimura *et al.* (1992) showed that DOM increased to approx. 300 mg L^{-1} after 15 days of submergence and declined to approx. 100 mg L^{-1} after 21 days. Tinh (1999) reported that DOM ranged between 100-220 mg L^{-1} in rice fields on acid sulphate soils. Decomposition of organic matter is much more rapid in tropical than in temperate soils (Tiessen, Cuevas & Chacon, 1994). This implies that in tropical soils, the concentration of trace metals in the soil solution could be markedly affected by changes in soil organic matter content after biosolids application (Ross, 1996; Appel & Ma, 2002).

Soil minerals

Besides specific sorption of trace metals, predominantly to humic compounds, soil inorganic matter including clay minerals, oxides and hydroxides also contributes to trace metal sorption (Kabata-Pendias & Pendias, 2001). Clay minerals may contain negligible amounts of trace metals as structural components, but their sorption capacity for trace metals plays an important role, especially in soils with low pH and where metal loading is high in comparison with the soil organic matter content (Weng, Temminghoff & van Riemsdijk, 2001). Strongly weathered soils differ from soils of temperate regions in both mineralogy and surface chemical properties. The former consist largely of sesquioxides and 1:1 layer silicate minerals (kaolinite), both of which have variable surface charge or pH-dependent charge, whereas soils in temperate regions are composed of clays with mostly permanent negative charge (McBride, 1994; Naidu, Sumner & Harter, 1998; Appel & Ma, 2002). Fluvisols are very young soils in which the parent material is mostly alluvial deposits of various origins and thus they may represent a variation in soil and clay mineralogy (Driessen & Dudal, 1989).

Several oxide minerals in soil, such as iron oxides and hydroxides, aluminium oxides and manganese oxides, are known to play a vital role in adsorption of trace metals (Hsu, 1989; McKenzie, 1989; Schwertmann & Taylor, 1989), especially for tropical soils, *e.g.* Ferralsols (Appel & Ma, 2002; Silveira *et al.*, 2006). Adsorption on oxide minerals may depend on pH because of changes in both the speciation of the metal in solution and the nature of the adsorbent. Variable-charge mineral surfaces become more negatively charged with increasing pH, and surface groups which have lost protons may be able to adsorb metals more readily from solutions (Stumm, Hohl & Dalang, 1976). For example, metal adsorption to Al hydroxides changes from little adsorption to complete adsorption over a narrow range of pH (Hsu, 1989; Al-Abadleh & Grassian, 2003). Iron oxides may be present in various crystalline forms. However, most ion adsorption studies have been carried out on the two most common minerals, goethite and haematite, but since all their oxides have similar hydroxylated surfaces and pH-dependent charges, they could be expected to display similar affinities toward the respective ions (Schwertmann & Taylor, 1989). Manganese oxides also possess a pH-dependent surface charge. Trace metals are generally adsorbed by Mn oxides in the order Pb>Cu>Mn>Zn (McKenzie, 1989).

The formation of trace metals with some soil inorganic ligands (*e.g.* CO_3^{2-}, S^{2-}) may cause precipitation. However, for most trace metals, precipitation is less likely than chemisorption because of their low concentration in the soil (McBride, 1994). An exception might be the formation of sulphides during the flooded (reduced) conditions that are common in paddy systems in the tropics. Street, Ladsay & Sabey (1977) found that precipitation of $CdCO_3$ or $Cd_3(PO_4)_2$ may occur at high Cd concentrations (>0.01 mg L^{-1}) in the soil solution. However, Holm, Andersen & Christensen (1996) concluded that under environmentally relevant conditions, carbonates are not likely to govern aqueous Cd concentrations in calcareous agricultural soils.

Modelling metal binding

Simple models

In the simplest possible approach, the relationship between dissolved metals and adsorbed metals in the soil can be explained by the linear K_d model (Eq. 1) or by the Freundlich equation (Eq. 2):

$$K_\mathrm{d} = \frac{(\text{Adsorbed metal})}{(\text{Dissolved metal})} \qquad \text{(Eq. 1)}$$

$$K_\mathrm{F} = \frac{(\text{Adsorbed metal})}{(\text{Dissolved metal})^m} \qquad \text{(Eq. 2)}$$

where K_d is the distribution coefficient for the linear K_d model (Eq. 1), K_F is the Freundlich coefficient and m is a dimensionless empirical constant (the Freundlich non-ideality parameter). The adsorbed metal concentration is usually given in mg kg^{-1} and the dissolved metal concentration in mg L^{-1}. Therefore, the units for the K_d and K_F (distribution coefficients) values are in L kg^{-1} (m=1 for the Freundlich equation) or mg^{1-m} L^{m} kg^{-1} for K_F if m differs from 1. If it could be assumed that the ratio of the total contaminants bound to the solids relative to that found in the solution phase is constant, there would be a linear relationship between a dissolved metal and its adsorbed concentration.

From a purely theoretical perspective, K_d is auto-correlated to the adsorbed soil metal content (since it is equivalent to the numerator of the ratio, see Eq. 1). The Freundlich non-ideality parameter m was found to vary from ~0.4 to ~1.5 for 15 different chemical elements in a study of 11 soils in the USA (Buchter *et al.*, 1989), suggesting that different elements have different sorption properties. In the low concentration range, the Freundlich equation may be simplified to a linear relationship (m=1). Alumaa *et al.* (2002) reported that the K_d value for Cd may vary within a wide range, from 57 to 63 000 L kg^{-1}. Sauvé, Hendershot & Allen (2000) demonstrated that two divalent metals (Pb, Zn) react in opposing ways to increased concentration. Larger quantities of Pb in solution promote its relative adsorption and increase the K_d. Conversely for Zn, higher concentrations of Zn decrease the K_d, reflecting a lowered affinity of the solid phase for Zn as it moves toward saturation. Sauvé, Hendershot & Allen (2000) used multiple linear regression analysis and found that the partitioning coefficients (K_d) were best predicted using empirical linear regressions with pH alone or pH and either the log of SOM or the log of total soil metal concentration. Hence, the total concentration alone is not sufficient to explain the solubility of metals in the soil solution.

Modelling metal binding to organic matter

Several different modelling approaches have been developed to comprehensively describe competitive ion binding to natural organic matter (Benedetti *et al.*, 1995). Some of the models take into account chemical heterogeneity of HS, variable stoichiometry of binding, competition between specifically bound ions and electrostatic effects that influence non-specific binding of counter-ions. Currently, the most widely used models for organic complexation are Model VI and NICA-Donnan (Kinniburgh *et al.*, 1996; Tipping, 1998; Kinniburgh *et al.*, 1999). Gustafsson, Pechova & Berggren (2003) used the Stockholm Humic Model (SHM) to describe proton binding and dissolved metal concentrations in a variety of soils in boreal climates. They found that the organic matter is an important sorbent for metals in many surface horizons of soil, and the necessity of properly accounting for the competition from aluminium in simulations of dissolved metal concentrations was stressed.

NICA-Donnan model

The Non Ideal Competitive Adsorption Donnan (NICA-Donnan) model was developed to describe the competitive adsorption of ions by HS and is described in detail by Kinniburgh *et al.* (1999). In the model, the negative charge on the humic molecules gives rise to attraction of counter-ions, which accumulate in the vicinity of the molecules, inside the Donnan phase. The volume of the Donnan phase is given by the following relationship:

$$\log V_{\mathrm{D}} = b(1 - \log I) - 1 \tag{Eq. 3}$$

where V_{D} is the volume of the Donnan phase (dm^3 kg^{-1}), I is the ionic strength (M) and b is an empirical parameter that has been suggested to be 0.49 and 0.57 for the solid phase of HA and FA, respectively (Milne *et al.*, 2003). All of the charge on the humic particle, q (mol$_c$ kg^{-1}), is assumed to be completely neutralised by counter-ions within the Donnan volume. This leads to the following charge balance expression:

$$\frac{q}{V_{\mathrm{D}}} + \sum_i z_i (c_{\mathrm{D},i} - c_i) = 0 \tag{Eq. 4}$$

where $c_{\mathrm{D},i}$ is the concentration of component i with charge z_i in the Donnan volume and c_i is its concentration in the bulk solution. To model ion binding by soil humic material, a bimodal distribution of binding sites is assumed. The two binding sites represent a carboxylic ('weak') and a phenolic ('strong') site. The total amount bound of component i (Q$_i$) is given by the following equation:

$$\begin{aligned} Q_i = {} & \frac{n_{i1}}{n_{\mathrm{H1}}} \times Q_{\max 1} \times \frac{(\tilde{K}_{i1} . c_{\mathrm{D},i})^{n_{i1}}}{\sum_i (\tilde{K}_{i1} . c_{\mathrm{D},i})^{n_{i1}}} \times \frac{\left(\sum_i (\tilde{K}_{i1} . c_{\mathrm{D},i})^{n_{i1}}\right)^{p_1}}{1 + \left(\sum_i (\tilde{K}_{i1} . c_{\mathrm{D},i})^{n_{i1}}\right)^{p_1}} \\ & + \frac{n_{i2}}{n_{\mathrm{H2}}} \times Q_{\max 2} \times \frac{(\tilde{K}_{i2} . c_{\mathrm{D},i})^{n_{i2}}}{\sum_i (\tilde{K}_{i2} . c_{\mathrm{D},i})^{n_{i2}}} \times \frac{\left(\sum_i (\tilde{K}_{i2} . c_{\mathrm{D},i})^{n_{i2}}\right)^{p_2}}{1 + \left(\sum_i (\tilde{K}_{i2} . c_{\mathrm{D},i})^{n_{i2}}\right)^{p_2}} \end{aligned} \tag{Eq. 5}$$

where the subscripts 1 and 2 refer to sites 1 and 2, n_i reflects overall non-ideal behaviour of ion i and n_{H} the non-ideal behaviour of proton, $\tilde{K}_i$ is the median value of the affinity distribution for species i, p accounts for the intrinsic chemical heterogeneity of sorbent, and $Q_{\max}$ is the total site concentration (mol kg^{-1}).

Stockholm Humic Model

The SHM is an integral part of the chemical equilibrium model Visual MINTEQ (Gustafsson, 2001; Gustafsson, Pechova & Berggren, 2003; Gustafsson & van Schaik, 2003; Gustafsson & Berggren Kleja, 2005). The SHM is a discrete-site/electrostatic model in which the HA or FA is assumed to have eight proton-binding sites with different acid-base characteristics. In the model, the HS dissociation reaction is assumed as:

ROH $\Leftrightarrow$ RO$^-$ + H$^+$, K_i (Eq. 6)

where RO represents a binding site of the humic molecule (commonly a carboxylate or phenolate group). In the SHM, K_i is an intrinsic dissociation constant, which includes an electrostatic correction term. The definition of K_i is:

$$K_i = \frac{\{\mathrm{RO}^-\}\{\mathrm{H}^+\}}{\{\mathrm{ROH}\}} e^{-g_f \cdot \frac{F\psi_0}{RT}} \qquad \text{(Eq. 7)}$$

where F is the Faraday constant, R the gas constant, T the absolute temperature, ψ_0 is the potential in the *0*-plane (*i.e.* at the surface), and g_f is the 'gel fraction' parameter, which takes a value between 0 and 1. The g_f value reflects the proportion of the humics that are aggregated in gel-like structures; electrostatic corrections are only made for this part. In a survey of nine FA and nine HA, it was found that the g_f value varied between 0.45 and 1, with an average of 0.78 (Gustafsson, 2001).

The SHM uses a discrete-site approach to describe the pH dependence of HS dissociation. There are eight ROH sites of different acid strengths and so there are eight K_i values. The four most strongly acidic sites (i = 1-4) are referred to as type A sites, whereas sites 5-8 are type B sites. The most strongly acidic sites probably represent mainly carboxylate groups, whereas the type B sites are thought to represent weaker acids such as phenolic acids. Four constants (logK_A, logK_B, ΔpK_A and ΔpK_B) are needed to define the eight log K_i values, according to:

$$i = 1\text{-}4, \quad \log K_i = \log K_A - \frac{(2i-5)}{6}\Delta pK_A \qquad \text{(Eq. 8)}$$

$$i = 5\text{-}8, \quad \log K_i = \log K_B - \frac{(2i-13)}{6}\Delta pK_B \qquad \text{(Eq. 9)}$$

The total amount of proton-dissociating sites n (mol g^{-1}) is the sum of all type A and B sites. Within each site group (A or B) all sites are present in equal amounts but the partitioning between type A and B groups may vary, depending on the nature of the humic sample. In Gustafsson (2001) it was assumed that for fulvic acids, the total amount of type B sites was 30% of the amount of type A sites, whereas for humic acids, the amount of type B sites was assumed to be 50% of type A sites.

Diffuse Layer Model and Gaines-Thomas equation

The Diffuse Layer Model (DLM) is the simplest complexation model to describe metal binding to oxide surfaces. Application of DLM to describe ion adsorption onto the hydrous ferric oxide (HFO) surface is described detail by Dzombak &

Morel (1990). This model considers the pH-dependent specific adsorption of metal ions and protons on the mineral surface. The model assumes the presence of two types of surface sites: one group of high-affinity sites ($Fe^{s}OH$) and one group that has a weaker affinity to complex metals ($Fe^{w}OH$). The surface concentration of the high-affinity site is 0.056 sites nm^{-2} and that of the weak site 2.25 sites nm^{-2}. The proton affinity of the two types of sites is the same. The reactions for divalent trace metal (Me^{2+}) such as Cd, Cu, Pb, Mn, and Zn are described in Eq. 10-11 and for Cr^{3+} in Eq. 12 (Dzombak & Morel, 1990). The surface complexation constants for the HFO are given in Table 2.

$$\equiv Fe^{s}OH^{0} + Me^{2+} \Leftrightarrow \equiv Fe^{s}OMe^{+} + H^{+} \quad K_1 \qquad \text{(Eq. 10)}$$

$$\equiv Fe^{w}OH^{0} + Me^{2+} \Leftrightarrow \equiv Fe^{w}OMe^{+} + H^{+} \quad K_2 \qquad \text{(Eq. 11)}$$

$$\equiv Fe^{s}OH^{0} + Cr^{3+} + H_2O \Leftrightarrow \equiv Fe^{s}OCr^{2+} + 2H^{+} \quad K_1 \qquad \text{(Eq. 12)}$$

Table 2. *Surface complexation constants for hydrous ferric oxides (Dzombak & Morel, 1990)*

	H^{+}	Cd^{2+}	Cr^{3+}	Cu^{2+}	Pb^{2+}	Mn^{2+}	Zn^{2+}
$\log K_1$	7.29	0.47	2.06	2.89	4.65	-0.4	0.99
$\log K_2$	-8.93	-2.90	--	0.6	0.3	-3.5	-1.99

The clay mineral surface can attract dissolved ions by exchange reaction. To determine the partitioning between different ions for the available surface charge, the Gaines-Thomas exchange equation may be used (Gustafsson, 2007). To describe the cation exchange equilibrium of a sorbed ion A exchanged for ion B, the equation is written as:

$$K_{GT} = \frac{E_B^{1/m}\{A\}^{1/n}}{E_A^{1/n}\{B\}^{1/m}} \qquad \text{(Eq. 13)}$$

where *n* is the charge of ion A and *m* the charge of ion B, and E_A and E_B are the charge equivalent fractions of the cation exchange capacity which consist of sorbed ion A and sorbed ion B (mol_c/mol_c).

The Gaines-Thomas equation produces a high selectivity of bi- and trivalent ions over monovalent ions. This may give a fairly realistic description on colloid surfaces with a high density of charged groups (*e.g.* clays with a lot of fixed charge) because multivalent ions may be attracted to an appropriate number of surface charges (Gustafsson, 2007).

Risk assessment of trace metals in the environment

The effects of potentially harmful contamination are usually described as environmental hazard and environmental risk (Janssen *et al.*, 2000). Hazard is an inherent property of a substance and hence the potential to cause an adverse effect, whereas risk is the statistical probability that the hazard will actually occur (Dudka & Miller, 1999). Two main methods of assessing hazard exposure and risk are experimental tests, *e.g.* ecotoxicology tests, and simulation modelling (Ross, 1996; Janssen *et al.*, 2000; Lock & Janssen, 2001; Landner & Reuther, 2004).

Trace metals may pose risks to the environment. At present, these risks are being managed through the establishment of environmental quality criteria and standards (Janssen *et al.*, 2000). Environmental quality criteria are intended to define, on the basis of sound scientific information and toxicological principles, concentrations of specific chemicals in the environment that are protective of terrestrial and aquatic life and the human food chain (*e.g.* McLaughlin & Singh, 1999; Janssen *et al.*, 2000; Zarcinas *et al.*, 2004; Pruvot *et al.*, 2006; Chaudri *et al.*, 2007). In order to ensure safe quality of food products, it is essential to standardise the allowable loading of contaminants to agricultural land (Landner & Reuther, 2004). Therefore the estimation of metal loads to agricultural land is necessary. A field (soil surface) element balance can be a good tool to estimate the input/output and the accumulation rate of trace elements, and thus predict the time to reach the maximum allowable concentration (MAC) with the present metal load (*e.g.* Öborn *et al.*, 2003).

Thresholds

Threshold limits of trace metals in agricultural soil have been set by directives in various countries (Table 3). However, these threshold limits differ greatly depending on the local conditions, as well as the basis on which they have been derived (McGrath *et al.*, 1994; Ross, 1996; Janssen *et al.*, 2000).

Risks associated with metal contamination in soils are difficult to assess (Nolan, Lombi & McLaughlin, 2003; Nolan, Zhang & McLaughlin, 2005). Although threshold values are intended to be used as an indicator of the risk and degree of contamination (SEPA, 1996), the bioavailability of trace metals, their biological uptake and ecotoxicological effects on the soil biota can be better understood in terms of their chemical speciation rather total concentration (Sauvé, Hendershot & Allen, 2000; Landner & Reuther, 2004; van Laer *et al.*, 2006). It is recognised that the important pathway for transfer of metals to plants is through the soil solution (Figure 1). In addition, the uptake of metal ions by plants, microorganisms or soil fauna is usually related to free metal-ion activity. Therefore, risk assessment of trace metals in soils requires an assessment of the proportion of the total metal that is in mobile, free metal and possibly bioavailable form (Landner & Reuther, 2004). In addition, total concentrations do not provide accurate information related to leaching of trace metals (Holm *et al.*, 1998).

Table 3. *Maximum allowable concentration (mg kg^{-1}) of Cd, Cu, Pb and Zn in agricultural soil in some individual countries and in the European Union (EU)*

Country	Element				Source
	Cd	Cu	Pb	Zn	
Australia	1	100	150	200	McLaughlin *et al.* (2000)
Canada	0.5	30	25	50	IAEA (2004)
China	0.3	50	250	200	SEPAC (1995)
Denmark	0.3	30	40	100	IAEA (2004)
EU[a]	1-3	50-140	50-300	150-300	EC (1986)
Germany[b]	0.4-1.5	20-60	40-100	60-200	IAEA (2004)
Finland	0.3	32	38	90	IAEA (2004)
France[c]	2	100	40	300	Johansson *et al.* (1997)
Netherlands[d]	0.8	36	85	140	McLaughlin *et al.* (2000)
Norway	1	50	50	150	Haiyan & Stuanes (2003)
Sweden[c,e]	0.4	40	40	100 (150)	SNFS (2005)
UK[c]	3	135	30	300	Johansson *et al.* (1997)
US[f]	20	750	150	140	McGrath *et al.* (1994)
Vietnam	2	50	70	200	MOST (2002)

[a] For agricultural soil (pH = 6-7) where application of sewage sludge is intended.
[b] The first value is for sandy soil, second value for clay soil.
[c] For agricultural soil where application of sewage sludge is intended.
[d] Standard soil of 25% clay, 10% organic matter. Element concentrations are normalised on the basis of clay (L) and organic matter (H) content of soil ($Cd=0.4 + 0.007\times[L+3H]$; $Cu=15 + 0.6\times[L+H]$; $Pb=50 + [L+H]$; $Zn = 50 + 1.5\times[2L+H]$).
[e] Value in brackets refers to only some parts of Sweden.
[f] Calculated from maximum cumulative pollutant loading limits without taking into account background concentration of the elements in soils.

Metal losses by leaching and surface runoff

Outputs of trace metals from agricultural soils include leaching, surface runoff, erosion and removal through crop products (Figure 1). Although data on trace metal leaching and runoff are essential information to evaluate the trace metal flows from agricultural soil into groundwater or surface water, such data are very scarce (Bengtsson *et al.*, 2006). Factors that affect metal leaching losses may include certain soil properties (*e.g.* any property that affects metal solubility and mobility, soil structure included), ambient conditions (*e.g.* agricultural practice, precipitation, temperature, *etc.*), and chemical properties of the metal in question (Sahuquillo, Rigol & Rauret, 2003; McLaren *et al.*, 2004). The annual metal leaching losses at field level can be estimated either indirectly using a mass balance approach or directly by collecting and analysing drainage water (Bengtsson *et al.*, 2006).

Holm *et al.* (1998) estimated the leaching output from 15 contaminated soils by collecting and analysing drainage water that had been displaced through small plant pots (13 cm diameter). They estimated the leaching losses to be 0.5-17 g Cd ha^{-1} yr^{-1} and 9-3600 g Zn ha^{-1} yr^{-1}, corresponding to approximately 0.1% of the total soil content of Cd and Zn per year. The metal concentrations measured in the leachate correlated fairly well with the concentrations measured in 10^{-2}M

$Ca(NO_3)_2$ soil extracts and the authors concluded that the method could be used for estimating the amounts of Cd and Zn being leached from the soil.

Bengtsson *et al.* (2006) used suction cup lysimeters to collect soil water at several soil depths directly in the field during a five-year period in order to determine metal concentrations in the soil solution in non-contaminated agricultural soils. They estimated the water fluxes at the sites by applying a dynamic hydrological model. The losses through surface runoff were 0.13 ±0.09 g Cd ha^{-1} yr^{-1}, 43±18 g Cu ha^{-1} yr^{-1} and 16 ±9 g Zn ha^{-1} yr^{-1}, while the leaching from the rooting zone was 0.22 ±0.20 g Cd ha^{-1} yr^{-1}, 50±33 g Cu ha^{-1} yr^{-1} and 24 ±20 g Zn ha^{-1} yr^{-1}.

Human exposure

Non-sustainable development increases trace metal fluxes. The increasing number of chemicals present in the residential and occupational environment elevates the risk of human exposure to potentially toxic metals. Contaminants can be applied to soils, enter water supplies directly, or fall directly onto, or be absorbed by, vegetation. Once in the soil, contaminants can leach and move to surface water and groundwater, or be lost from the soil in surface runoff (Pierzynski, Sims & Vance, 2005).

Cadmium, for example, is readily taken up by plants and food chain transfer is the primary route of exposure (Gupta, 2006). Rice grain Cd concentration in samples collected in an area downstream from an actively mined zone of Zn minerals in western Thailand ranged from 0.05 to 7.7 mg Cd kg^{-1}, with over 90% of rice grain samples containing Cd at concentrations exceeding the maximum permissible level for rice grain of 0.2 mg kg^{-1} (EC, 2001) or 0.4 mg kg^{-1} (FAO/WHO, 2006) (Simmons *et al.*, 2005). The disease *itai-itai* in Japan (Jinzu river basin) resulted from long-term exposure to Cd-enriched rice (Morishita, 1981). In that study, Morishita (1981) reported that the average rice grain Cd concentration ranged from 0.41 to 0.93 mg kg^{-1} and that the lowest concentration occurring was 0.3 mg kg^{-1}. Hellström *et al.* (2007) studied Cd exposure pathways in populations living near a nickel-cadmium battery plant and found that consumption of locally grown vegetables and root crops was an important exposure pathway for individuals, whereas direct exposure through ambient air was of less importance.

Copper and Zn are essential elements. The approximate daily Cu requirement is 0.2 mg in children below six months of age, increasing to approximately 0.9 mg for adults. In the US, the recommended dietary allowance of Zn is 2 mg d^{-1} for children below 6 months and 8-11 mg d^{-1} for adults (Reilly, 2004). Copper poisoning is often caused by excessive intake resulting from contaminated water supplies or food. The long-term effects can be serious, resulting in Cu-induced liver cirrhosis, especially in children (Tanner, 1998; Reilly, 2004). Zinc toxicity in humans is rare but it can occur through ingestion in large amounts, *e.g.* through ingestion of acidic drink or food stored in galvanised containers, or through inhalation of Zn oxide fumes (Gupta, 2006). Acute toxicity can be caused by consumption of 1 g or more and results in nausea, vomiting, diarrhoea, fever and lethargy. Chronic ingestion of high levels of 75-300 mg Zn d^{-1} in the form of dietary supplements has been shown to result in interference with the absorption of other trace elements, especially copper and iron (Reilly, 2004).

Cadmium and Pb are non-essential elements that can be toxic to humans (Järup, 2003; Reilly, 2004). Cadmium exposure may cause kidney damage, while long-term high Cd exposure may cause skeletal damage (*e.g.* Morishita, 1981; Järup, 2003). Symptoms of chronic exposure could include alopecia, anaemia, arthritis, learning disorders, migraines, growth impairment, emphysema, osteoporosis, loss of taste and smell, poor appetite and cardiovascular disease (Järup, 2003). Toxicity symptoms of Pb in humans include arrested growth of bones (Gupta, 2006). People who have been exposed to Pb for a long time may suffer from memory deterioration, prolonged reaction time and reduced cognitive ability (Järup, 2003).

Clearly, there are many factors that influence the intensity of exposure experienced by individuals, including age, sex, season, hand-to-mouth behaviour, occupation, socio-economic status, diet and cultural practices (Mielke & Reagan, 1998). Children are more susceptible to the potentially negative health effects of metals in soils than adults, both for physiological and behavioural reasons. The former may include *e.g.* negative effects on the central nervous system (Osman, 1998; Pierzynski, Sims & Vance, 2005). One such effect is impairment of mental development, which causes children with chronic exposure to Pb to score lower in IQ tests than non-exposed children. Children exhibit significant hand-to-mouth activity at a certain age and can consume considerable quantities of soil by that route (Ljung, 2006), or can indirectly consume soil through *e.g.* house dust (Reilly, 2004; Pierzynski, Sims & Vance, 2005).

Materials and Methods

Description of study sites

The Red River delta is located in northern Vietnam. The delta covers 11 provinces within an area of 1.48 million ha (4.5% of the total area of the country) with a population of 18 million (1218 people km^{-2}). The climate is of the monsoon type and is influenced by changes in tropical humidity. The annual rainfall is 1500-2000 mm, and more than 50% of the rainfall is concentrated to the period June-August. The mean monthly temperature varies between 17 and 29 ^{o}C, with the warmest period from June to August and the coldest during December and January. Rice is the principal crop in the delta, but beans, maize, potatoes, vegetables and subtropical crops are also grown.

The agricultural soils are mainly Fluvisols and Acrisols (Table 4) where the parent material is alluvial deposits. These soils consist mainly of sedimentary (sandstone, shale, schist) and metamorphic (clay, slate, phyllite, mica, gneiss) material. The latter may include acid magmatic rocks (rhyolite, granite and liparite).

Table 4. *Distribution of Fluvisols and Acrisols in the Red River delta, in the whole of Vietnam and in the world (FAO-ISRIC-ISSS, 1998; Ha et al., 2003; Ha et al., 2005)*

Soil	Red River	Vietnam	World
Fluvisols (10^3 ha)	600[a]	3 500[a]	350 000
Acrisols (10^3 ha)	150[a]	3 400[a]	1000 000
Total area (10^3 ha)	1 480	33 121	

[a] Fluvisols and Acrisols use for agricultural soils.

This study was carried out in peri-urban areas of four provinces in the Red River delta of Vietnam that include the cities of Hanoi, Nam Dinh, Ha Tay and Vinh Phuc (Figure 2).

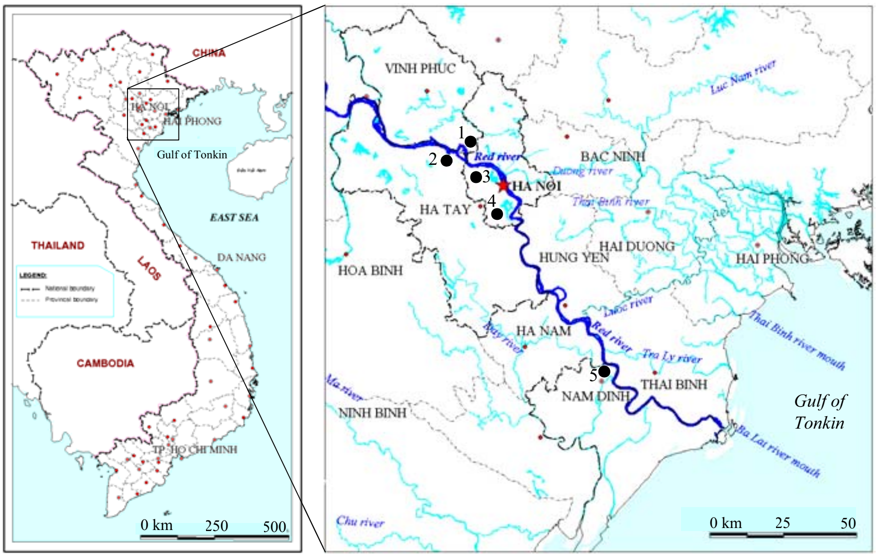

Figure 2. Map of Vietnam. The locations of the study sites are marked with black dots (●) including: 1) Vinh Phuc site, 2) Ha Tay site, 3) Hanoi upstream site (Tu Liem), 4) Hanoi downstream site (Thanh Tri) and 5) Nam Dinh site. Hanoi City centre is marked by a star (★)

The sites studied and the samples taken at the different sites are summarised in Table 5 with reference to the paper in which the work is presented.

Table 5. *Summary of the field study sites, field experiments and samples included in this thesis*

Study site	Description	Samples	Paper
Hanoi			
Thanh Tri district	Bang B village, wastewater reuse, aquatic vegetable production	8 soil, 33 irrigation water, 31 vegetable	I
	Bang B village, paddy rice field (Hoang Liet commune)	4 soil treated with wastewater	II
		6 wastewater	II
		1 soil treated with wastewater (TTBB)	III, IV
		1 soil profile[a]	
	Thanh Liet commune, paddy rice field	4 soil irrigated with river water	II
		4 river water	II
Tu Liem district	Phuc Ly village, biosolids application, dry-land vegetable production	18 soil, 25 irrigation water, 25 biosolid (chicken manure), 64 vegetable	I
Nam Dinh			
My Loc district	Hong Long cooperative, paddy rice field (My Tan commune)	8 soil treated with wastewater	II
		1 soil treated with wastewater (HL)	III
		5 wastewater	II
		1 soil profile[a]	
	Tan Tien cooperative, paddy rice field (My Tan commune)	8 soil irrigated with river water	II
		4 river water	II
Vinh Phuc			
Me Linh district	Biosolids trial, chicken manure applied with 6 levels (0-450% of local practice)[b]	6 soil with triplicate treatments in biosolids trial (BoMl-BoMl6)	II
		3 soil (BoMl1 (0%), BoMl4 (150%) and BoMl6 (450%))	III
		1 soil (BoMl1)	IV
		1 soil profile[a]	
Ha Tay			
Dan Phuong district	Biosolids trial, composted manure applied with 6 levels (0-450% of local practice)[b]	6 soil with triplicate treatments in biosolids trial (BoDp1-BoDp6)	II
		3 soil (BoDp1 (0%), BoDp4 (150%) and BoDp6 (450%))	III
		1 soil profile[a]	

[a] Soil samples were taken at six depths within the profile (0-20, 20-30, 30-40, 40-50, 50-60, 60-70 cm) with an auger. Soil profile properties are given in the beginning of the Results and discussion section and Table 9.

[b] Farmers usually apply biosolids at a rate of 20 t ha^{-1} yr^{-1} for chicken manure (fresh weight, fw); and 14 t ha^{-1} yr^{-1} for composted manure (composted pig manure mixed with rice straw) (fw). The experimental design only included one biosolids application at the beginning of experiment.

Hanoi sites (Papers I- IV)

Two peri-urban areas of Hanoi City were selected for the studies. One is located in Bang B village, Hoang Liet commune, Thanh Tri district, 10 km south of Hanoi centre (Papers I-IV) and the other is located in Phuc Ly village, Minh Khai commune, Tu Liem district, 10 km west of Hanoi centre (only in Paper I). At both sites, farmers have shifted from rice production to cash crops during recent decades and vegetable production is the main farming activity. The soils are Eutric

Fluvisols (Hoang Fagerström *et al.*, 2006). At the Phuc Ly site farmers specialise in dry-land vegetable production, which is intensive in terms of number of crops per year, inputs of manure and mineral fertiliser, and pesticide use. The water supply at the Phuc Ly site is natural river water obtained from the Red River. Bang B is located downstream from industries and urban settlements and here farmers specialise in both dry-land and aquatic vegetables. The water supply for the Bang B site consists of sewage from the Kim Nguu River, which receives wastewater from Hanoi City. In addition, in Thanh Liet commune, 3 km west of Hoang Liet commune, belonging to Thanh Tri district, rice fields irrigated by river water (Red River water) were selected as control sites (Paper II).

Nam Dinh site (Papers II, III)

The sewage irrigation study area is located in a peri-urban region downstream from Nam Dinh City, belonging to My Tan commune, My Loc district, Nam Dinh province (Trang *et al.*, 2006), 100 km south-east of Hanoi. In this area farmers have been using municipal wastewater for irrigation since the 1980s as a result of the increasing urbanisation. Soil samples were taken in the fields where the DANIDA-IWMI project '*Wastewater reuse in agriculture in Vietnam - a case study on wastewater-irrigated rice at Nam Dinh, Red River Delta, Vietnam 2001-2005'* was carried out in collaboration between the Royal Veterinary and Agricultural University, Denmark (KVL), the International Water Management Institute (IWMI), Bangkok, and the National Institute for Soils and Fertilisers, Vietnam (NISF). The soil type is Humi-Endogleyic Fluvisol (Eutric) according to WRB (FAO-ISRIC-ISSS, 1998). The soils are fertile and suitable for growing crops. Rice (*Oryza sativa* L.) has been the main crop in the area, but there is a tendency to convert from rice to vegetable production due to the demand from the inner city.

Ha Tay site (Papers II, III)

The study site is located in Dan Phuong district, Ha Tay province, 20 km north-west of Hanoi city. The soil is a Cambic Fluvisol (FAO-ISRIC-ISSS, 1998). At this site, a field experiment with different rates of biosolids application to agricultural systems was set up by NISF and CSIRO Land and Water Australia within an ACIAR-funded project (ACIAR Project N0.LWR1/1998/119) *'Impact of heavy metals on sustainability of fertilisation and waste recycling in peri-urban and intensive agriculture in south-east Asia'* (Stevens *et al.*, 2003b). A similar experiment was also set up in Vinh Phuc province (see below) The field trial involved application of six different levels of composted manure ranging from 0-450% of the level local farmers normally apply per year (14 metric tonnes ha^{-1}, 100%). The experiments had a randomised block design with triplicate treatments. Rice was grown at this site.

Vinh Phuc site (Papers II, III, IV)

The study site is located in Me Linh district, Vinh Phuc province, 25 km north of Hanoi city. The biosolids trial experiment was set up by the ACIAR-funded project mentioned above. The soil is a Haplic Acrisol (FAO-ISRIC-ISSS, 1998). The field trial involved application of six different levels of chicken manure ranging from 0-450% of the level local farmers normally apply per year (21 metric tonnes ha^{-1}, 100%). The experiments had a randomised block design with triplicate treatments. Vegetables were grown at this site, predominantly cabbage (*Brassica oleacea* L.) and squash (*Benicasa hispida* L.).

Sampling and sample preparation

Soil sampling was carried out in June 2004. The numbers of samples taken at different sites are listed in Table 5. Topsoil samples were taken to a depth of 0-20 cm using a stainless steel trowel (Paper I) or an auger (Paper II-IV). Three to five sub-samples were collected within a circle (2 m in diameter) in the treatments in the biosolids experiments and within areas of 25-250 m^2 at the other sites, and the sub-samples were bulked and mixed in the field. In addition, one soil profile at each study site was sampled at six different depths using a soil auger (Table 5). The soil samples were air-dried and crushed to pass through a 2 mm nylon sieve prior to analysis.

Manure samples (Paper I) (a minimum of five sub-samples) were collected and bulked just before each application event. The samples were air-dried and crushed to pass through a 2 mm nylon sieve prior to analysis.

Samples (consisting of at least five sub-samples) of vegetable material were collected at the time of harvest, rinsed with tap water and then washed thoroughly with distilled water. After air-drying samples were cut into small pieces, mixed evenly, dried to constant weight in an oven at 60-70 ^{o}C and finely ground to pass a 0.4 mm nylon sieve before digestion and chemical analysis (Paper I).

The dry matter content of fresh vegetable and manure samples was determined by drying at 105 ^{o}C as soon as possible after collection. Dry matter content of air-dried soil, manure and crop samples was also determined at 105 ^{o}C.

Irrigation water was sampled at the time of irrigation and subsequently stored in pre-washed (acid and distilled water) polyethylene bottles (Papers I & II). Rainwater was sampled once a week during the rainy season and on each significant precipitation event in the dry season (Paper I). After sampling a few drops of concentrated HCl were added to all water samples prior to chemical analysis.

Soil, water, fertiliser and crop analyses

The methods used to analyse soil, water, fertiliser and crop samples are summarised in Table 6, where references to the methods and to Papers I-IV are also given.

Soil pH was determined by inserting a combination electrode in a 1:5 (w:v) soil:water suspension. Total N in soil, manure (fresh sample) and plant samples was determined using the Kjeldahl procedure after digestion with concentrated H_2SO_4 (Paper I) or by LECO CHN analyser (Paper II, soil samples). Concentrated HNO_3 and H_2SO_4 digestion was used for total P and K. Humic (HA) and fulvic acids (FA) were extracted twice with 0.1 M NaOH and separated using methods described by Gustafsson & van Schaik (2003).

Soil bulk mineralogy was analysed by X-ray powder diffraction (XRDP) after milling of soil samples according to Hiller (1999). The mineralogical composition was quantified by full-pattern fitting as described in detail by Omotoso *et al.* (2006). Clay fractions of <2 μm were obtained by timed sedimentation and clay minerals identified were quantified using a mineral intensity factor approach based on calculated XRPD patterns as described by Hillier (2003).

Irrigation water samples were analysed for P, K, Cu, and Zn (Papers I & II), and Ca, Cd, Mg, Na, Pb (Paper II), and rainwater samples for P and K. Total N was quantified as the sum of four N forms: nitrate-N (NO_3^--N), nitrite-N (NO_2^--N), ammonium-N (NH_4^+-N) and organic-N (N_{org}). NO_2^--N and NO_3^--N were determined colorimetrically, NH_4^+-N was determined by a titration method after distillation of NH_3 into an acid solution, and N_{org} was determined by the macro-Kjeldahl method after subtraction of NH_4^+ (Eaton, Clesceri & Greenberg, 1995).

Table 6. *Summary of the methods used in this thesis*

Material/ topic studied	Specification	Method (Reference)	Paper
Soil analysis	Soil EC, pH_{H2O}, pH_{CaCl_2}	1:5 soil: solution ratio (Le *et al.*, 1996; Stevens *et al.*, 2003a)	I, II, III, IV
	Soil texture	Pipette method (Gee & Bauder, 1986)	III, IV
	Soil and clay mineralogy	Soil sample after grinding (Hillier, 1999) and clay was analysed by X-ray powder diffraction (Hiller, 2003; Omotoso *et al.*, 2006)	III
	Total N (N_{tot})	Kjeldahl procedure (Mickelson & Weaver, 1994)	I
	Total organic carbon (TOC) and N_{tot}	LECO CHN analyser (Leco CHN®CHN 932 analyser) after soil was dissolution of carbonates-C, and finely ground	II, III, IV
	Humic acid (HA) and fulvic acid (FA)	Extracted with 0.1M NaOH (2h) and separated by acidification to pH 2, TOC was analysed with Shimdzu TOC-5000 (Gustafsson & van Schaik, 2003)	III, IV
	Total P and K	Digested with concentrated HNO_3 and H_2SO_4 (Le *et al.*, 1996). P in the solution was determined colorimetrically (Eaton, Clesceri & Greenberg, 1995) and K by flame emission spectrometry	I
	Reverse *aqua regia* Cu, Zn	Digested with $3HNO_3$:HCl (Zarcinas, McLaughlin & Smart, 1996; Stevens *et al.*, 2003a) and using AAS (Perkin Elmer 3300)	I
	Reverse *aqua regia* Cd, Cu, Pb, Zn	Digested with $3HNO_3$:HCl (Zarcinas, McLaughlin & Smart, 1996; Stevens *et al.*, 2003a), using ICP-MS (Perkin Elmer ELAN 6100)	II, IV
	Ca, K, Mg, Na exchangeable	Extracted with 1M NH_4NO_3 (2h), 1:2.5 soil:solution ratio, using AAS (Perkin Elmer 300) and/or ICP-MS	II, III, IV
	Potentially soluble Cd, Cr, Cu, Mn, Pb, Zn	Extracted with 0.025 M Na_2H_2EDTA (1.5h), 1:10 soil:solution ratio (Streck & Richter, 1997), using ICP-MS	II, III, IV
	Amorphous Al, Fe	Extracted with 2.5% ascorbate (4h), 1:60 soil:solution ratio (Kostka & Luther, 1994), using ICP-OES (Jobin Yvon JY24)	III, IV
	Crystalline plus non-crystalline Al, Fe	Extracted with 1.7% sodium dithionite (16h), 1:60 soil:solution ratio (van Reeuwijk, 1993), using ICP-OES (Jobin Yvon JY24)	III, IV
Water analysis	Total N, P	Using methods described by Eaton, Clesceri & Greenberg (1995)	I, II
	K	Flame emission spectrometry	I
	Cu, Zn	Using AAS (Perkin Elmer 3300)	I
	Ca, Cd, Cu, Pb, K, Na, Mg	Using ICP-MS	II
Manure analysis	Total N	Kjeldahl procedure (Mickelson & Weaver, 1994)	I
	Total P and K	Digested with concentrated HNO_3 and H_2SO_4 (Le *et al.*, 1996). P in the solution was determined colorimetrically (Eaton, Clesceri & Greenberg, 1995) and K by flame emission spectrometry	I
	Reverse *aqua regia* Cu, Zn	Digested with $3HNO_3$:HCl (Zarcinas, McLaughlin & Smart, 1996; Stevens *et al.*, 2003a) and using AAS (Perkin Elmer 3300)	I
Crop analysis	Total N	Kjeldahl procedure (Mickelson & Weaver, 1994)	I
	Total P, K	Digested with concentrated HNO_3 and H_2SO_4 (Le *et al.*, 1996). P in the solution was determined colorimetrically (Eaton, Clesceri & Greenberg, 1995) and K by flame emission spectrometry	I
	Total Cu, Zn	Digested with concentrated HNO_3 and $HClO_4$ (Le *et al.*, 1996), using AAS (Perkin Elmer 3300)	I
Batch studies	Dissolved organic carbon (DOC)	Analysed with Shimdzu TOC-5000	III
	Cl^-, PO_4^{3-}, SO_4^{2-} solubility at equilibrium	Using ion chromatography (Dionex ICP-90)	III
	Al, Ca, Cd, Cr, Cu, Fe, K, Mg, Mn, Na, Pb, Zn solubility at equilibrium	Using ICP-MS	III

Element balance calculation (Paper I)

Element balance calculations at field level were used to demonstrate the nutrient flows in peri-urban agricultural systems including the major management-related input and output flows. The study was carried out at two sites downstream and upstream of Hanoi, respectively. Two vegetable plots in Thanh Tri district, Bang B village (BB1, BB2), and another two plots in Tu Liem district, Phuc Ly village (PL1, PL2), were monitored to quantify the element fluxes (*F*), which were estimated by multiplying the mass of material by their element concentrations (Eq. 14).

$$F = \sum_{i=1}^{n} Q_i . C_i \qquad \text{(Eq. 14)}$$

where *F* is the total element flow (input or output) over the period of measurement, *n* is the number of events (application of fertiliser, irrigation water, rain, or removal of harvested crop products, ect.), Q_i is the mass value of raw material at event *i* and C_i is concentration of calculated element in raw material at event *i*.

The annual element balance (Balance_E) was estimated from the main input and output flows. The equation below was used (Eq. 15); a more detailed explanation is given in Paper I.

$$\text{Balance}_\text{E} = S_\text{E} + \text{IW}_\text{E} + \text{RW}_\text{E} + F_\text{E} - H_\text{E} \qquad \text{(Eq. 15)}$$

where S_E is the input of element E from seedlings, IW_E the input in irrigation water, RW_E the input in rainwater (only N, P, and K), F_E the input in fertilisers and H_E is the output of element E from harvested crops. Methods used to estimate the input and output flows are summarised in Table 7. Trace metal input through atmospheric deposition was not included in the field balance due to lack of appropriate equipment for sampling and analyses. No relevant secondary data on metal input through atmospheric deposition could be found. For similar reasons, outputs through surface run-off and leaching losses were not included in the field balance calculations. Hence the inputs as well as the outputs were underestimated.

Table 7. *Methods to estimate the input and output flows in the field balances*

Flow	Mass value	Concentration
Seedlings	Seedlings weighed just before transplanting in the field	Analyses
Chicken manure, Horn, Ash	Amount weighed on every occasion of application	Analyses
NPK, Urea, P-fertiliser, K-fertiliser	Amounts weighed on every occasion of application	As stated by manufacturer
Irrigation water	Level of water on the field (Bang B) measured before and after irrigation or number of buckets (Phuc Ly) recorded.	Analyses
Rainwater	Data from weather stations (either Lang 10 km north of Bang B or a site adjacent to Phuc Ly)	Analyses
Harvested crop products	Estimated by either weighing every 10th bunch or weighing material removed from 3 x 0.25 m^2 areas, multiplied by number of bunches or total crop area harvested.	Analyses

Batch studies (Paper III)

To determine the extent of sorption at different soil pH, various amounts of acid (HNO_3) or base (NaOH) were added to soil samples (2 g) in centrifuge tubes, so that each soil was studied at eleven different pH values (in duplicate). Additional $NaNO_3$ salt was added to produce an ionic strength of approximately 0.02 M. The final volume of solution in the centrifuge tubes was 30 mL. The tubes were then equilibrated for 7 days at 20 °C prior to analyses. The supernatant was taken for pH measurement and analysed for DOC, anions (Cl^-, SO_4^{2-}, PO_4^{3-}) and dissolved metals (Al, Ca, Cd, Cr, Cu, Fe, K, Mg, Mn, Na, Pb, and Zn).

Modelling metal binding

It was assumed that three reactive surfaces could describe the adsorption behaviour of the soil. These three surfaces were Fe/Al (hydr)oxide, soil organic matter (SOM) and phyllosilicate clay. Multi-surface (MS) models were used to describe metal binding in the agricultural soils. These models combine the DLM for surface complexation to oxides, the SHM (Gustafsson, 2001) or the NICA-Donnan model for complexation to organic matter (Weng, Temminghoff & van Riemsdijk, 2001), and the Gaines-Thomas equation for simulation of ion exchange to clay minerals. Two MS models were used, the MS-DSGM and MS-DNGM models, and the difference between the models was that the former used the SHM to describe metal binding onto SOM, whereas MS-DNGM used the NICA-Donnan model. Both models used the DLM for oxide adsorption and the Gaines-Thomas equation for ion exchange. To apply the models, we used the chemical equilibrium programme Visual MINTEQ (Gustafsson, 2007), which also contains relevant solution complexation constants.

Binding to Fe/Al (hydr)oxide: To take surface complexation to Fe (hydr)oxide surfaces into account, the DLM (Dzombak & Morel, 1990) was used for specific binding of metal cations and (oxy)anions to hydrous ferric oxide (HFO). The recommended specific surface area of 600 m^2 g^{-1} for HFO was used to calculate site concentrations for the amorphous Fe and Al (hydr)oxides (Dijkstra, Meeussen & Comans, 2004). The total amount of amorphous Fe (hydr)oxides was calculated from Fe extracted with ascorbate and represented by HFO in the model. The amount of crystalline Fe (hydr)oxides was calculated from the difference between Fe-dithionite and Fe-ascorbate. However, site concentrations of crystalline Fe (hydr)oxides were calculated using a specific surface area of 100 m^2 g^{-1} (Dijkstra, Meeussen & Comans, 2004) and therefore to include crystalline Fe (hydr)oxides in the model, the suspension density of crystalline Fe (hydr)oxides was converted to HFO equivalents by dividing it by 6. In addition, amorphous Al (hydr)oxides were considered, for which HFO was taken as a surrogate sorbent in the model (Dijkstra, Meeussen & Comans, 2004). This contribution was calculated from Al extracted with dithionite citrate.

The SHM (Paper III) and the NICA-Donnan model (Paper III, IV) were used to examine binding to SOM. Measured DOC concentrations were used as input in the model, and in the SHM it was assumed that all DOC could be considered to be dissolved FA (Gustafsson *et al.*, 2007). In the NICA-Donnan model, it was assumed that the ratio between HA and FA was 1:1.

Binding to phyllosilicate clay minerals: The Gaines-Thomas equation was used to simulate ion exchange to phyllosilicate clays. To estimate the cation exchange capacity of the latter (CEC_{clay}, $cmol_c$ kg^{-1}), soil samples from the C horizon of the Acrisols (60-70 cm depth, where the TOC was low) were analysed for the cation exchange capacity (CEC_{soil}, $cmol_c$ kg^{-1}), TOC (%) and clay fraction (% of particle size <2 μm, pipette method). The CEC_{clay} for these C horizons were calculated from the equation below (van Reeuwijk, 1993), and the resulting CEC_{clay} was assumed to be valid also for the A horizon.

$$\mathrm{CEC}_{\mathrm{clay}} = \frac{100}{\mathrm{Clay}} \times \left(\mathrm{CEC}_{\mathrm{soil}} - 3.5 \times \mathrm{TOC}\right) \qquad \text{(Eq. 16)}$$

For the Fluvisols, CEC_{clay} was taken from literature data as 10 $cmol_c$ kg^{-1} (Nguyen *et al.*, 2001).

Scenarios (Paper IV)

Four scenarios (A-D) were set up and run for each soil order, *i.e.* Acrisols and Fluvisols (Table 8). The predicted soluble metal concentrations were compared with, and discussed in relation to, water quality standards. The variation in SOM and/or pH used in scenarios B, C, and D were within the range recorded in the Vietnamese soil inventory of Fluvisols (Ha *et al.*, 2003) and Acrisols (Ha *et al.*, 2005). For simplicity, the fraction of potentially soluble metals of the total metal loading (f_M) was assumed to be 0.5 (scenarios B and D). In scenario A, it was set to 0.1, 0.5 and 1.0. In scenario C, the value obtained by EDTA extraction was used. The soil:water ratio was assumed to be 1:1.

Table 8. *Scenarios for the effects of metal (Cd, Cu and Zn) loading, soil organic matter (SOM) and pH on metal solubility in Acrisols and Fluvisols*

Scenario	Metal	SOM	Soil pH
A	Loading up to MAC[a]	Current SOM content in the study soils: Fluvisols 3.2% Acrisols 1.8%	Current pH in the study soils: Fluvisols 6.6 Acrisols 6.1
B	Loading up to MAC[a] (similar to A)	Fluvisols 0.6 to 7.6% Acrisols 0.2 to 4.6%	Current pH in the study soils (similar to A): Fluvisols 6.6 Acrisols 6.1
C	At current level in the study soils (Cu, Zn, Cd) Fluvisols: 26, 78, 0.15 mg kg^{-1} Acrisols: 9, 44, 0.03 mg kg^{-1}	Fluvisols 0.6 to 7.6% Acrisols 0.2 to 4.6% (similar to B)	Fluvisols 4.3 to 6.6 Acrisols 3.8 to 6.1
D	Metal concentrations set to MAC[a]	Fluvisols 0.6 to 7.6% Acrisols 0.2 to 4.6% (similar to B)	Fluvisols 4.3 to 6.6 Acrisols 3.8 to 6.1 (similar to C)

[a]Maximum allowable concentrations (MAC) for agricultural soils in Vietnam are: 2 mg Cd kg^{-1}, 50 mg Cu kg^{-1}, 200 mg Zn kg^{-1} (MOST, 2002)

Statistical analyses

Data on the quantity of irrigation water and on element concentrations in crops, manure, irrigation water and rainwater (Paper I) were analysed by one-way ANOVA using plot (field) as a factor. Data from the experiments (Paper II) were analysed using the General Linear Model (GLM) procedure of Minitab Software version 14.0 (Minitab, 2003). Treatment means that showed significant differences at the probability level of $P<0.05$ were compared using Tukey's pairwise comparison procedure. In the wastewater study (Paper II), the source of irrigation water within the site (wastewater and river water) was used as a factor in the model, whereas biosolids application was used as factor in the biosolids field trials. The statistical model used was $y_{ij} = \mu + \alpha_i + e_{ij}$, where μ is the mean value for all treatments, α_i the difference between mean value of treatment *i* with overall mean, and e_{ij} is the random error.

Result from the biosolids trials (Paper II) were also analysed by regression analysis to assess the relationship between concentrations of elements in the soil (TOC, N_{tot}, trace metals) and the amount of biosolids applied. The statistical regression model was: $y_{ij} = a + bx_i + e_{ij}$, where y is the concentration of elements, a the intercept, b the slope of y_i against the corresponding value of y_i, x_i the level of biosolids application rate and e_{ij} is the random error effect.

In Paper III, the measured and simulated metal concentrations were compared through calculation of root-mean square errors (RMSEs). Because many of the metal determinations at small equilibrium concentration were uncertain due to analytical limitations, data points with observed concentrations $< 3.6 \times 10^{-10}$ M Cd, $< 3.9 \times 10^{-9}$ M Cr, $< 6.3 \times 10^{-9}$ M Cu, $< 3.6 \times 10^{-8}$ M Mn, $< 1.9 \times 10^{-9}$ M, Pb and $< 3.1 \times 10^{-8}$ M Zn were not included in the calculation of RMSEs.

Results and discussion

Soil properties

Some chemical and physical properties of the soil profiles in the study areas are presented in Table 9. The soils at the study sites were classified as Fluvisols at Hanoi (Eutric Fluvisol), Nam Dinh (Humi-Endogleyic Fluvisol) and Ha Tay (Cambic Fluvisol) and as Acrisols at Vinh Phuc (Haplic Acrisol) using the WRB system (FAO-ISRIC-ISSS, 1998). The soil pH was slightly acid (6.0-6.6). The soil organic carbon content in the topsoil (Ap horizon, 0-20 cm) of the Vinh Phuc soil (Acrisols) was lower than that of the other soils (Fluvisols). Soil organic carbon was highest in the topsoil layer and decreased with increasing soil depth. The soil organic carbon (TOC) in the subsoil (20-70 cm) in the Nam Dinh soil was higher than that of the other soils. Soil CEC in the topsoil and 60-70 cm layer of Vinh Phuc soil was lower than that of the other soils.

The clay content (fraction less than 2 μm diameter) in the Acrisols was 12%, which was lower than for the Fluvisols, where the clay content varied between 23 and 45%. The clay content at 60-70 cm depth in the soils was higher than that of the topsoil (except in Nam Dinh). The clay fraction was dominated by expandable clays followed by illite, the illite being higher in the Fluvisols (30-40%) and the expandable clays relatively more abundant (>70%) in the Acrisols. The expandable clays were all highly illitic mixed-layer illite-smectite and/or illite-vermiculite types, such as may be produced by the weathering of mica. Muscovite mica was an important component of the bulk samples, which further suggests that the expandable clays may be weathering products of mica (Paper III).

The concentrations of reverse *aqua regia*-extractable (Rev *Aq Reg*) trace metals exhibited a trend of being highest in the topsoil and the 20-30 cm layer. This indicates the accumulation of trace metals in the surface layers, which could be explained by anthropogenic inputs including fertilisers, irrigation water and perhaps also atmospheric deposition.

Table 9. *Selected properties of soil profiles in the study areas. Soil profiles at the Hanoi and Nam Dinh sites were taken in wastewater-irrigated rice fields, while the soil profiles at the Ha Tay and Vinh Phuc sites were taken in the control plot in the biosolids trials (no application of biosolids)*

Site/soil unit (soil type)	Depth (cm)	pH_{H2O}	TOC[a]	CEC[b]	Soil texture[c]	Clay[d]	Clay composition[e]				Trace metal[g]			
							Chlorite	Kaolinite	Illite	Expandable[f]	Cd	Cu	Pb	Zn
Hanoi/Fluvisols	0-20	6.63	1.56	7.4	23/40/37	24	6	5	32	57	0.153	26.5	24.6	77.8
(Eutric Fluvisol)	20-30		0.58								0.161	24.6	24.2	83.8
	30-40		0.63								0.156	23.7	21.5	81.5
	40-50		0.48								0.152	23.9	19.7	80.0
	50-60		0.57								0.153	24.3	20.2	74.6
	60-70		0.34	10.6	31/33/36						0.095	23.5	19.8	73.0
Nam Dinh/Fluvisols	0-20	6.14	2.66	10.6	45/43/12	46	6	7	40	47	0.173	39.8	41.9	112.9
(Humi-Endogleyic	20-30		1.99								0.184	38.8	42.3	116.3
Fluvisol)	30-40		1.71								0.143	33.4	38.5	106.3
	40-50		1.38								0.149	34.5	38.7	108.2
	50-60		1.35								0.133	34.3	38.4	105.9
	60-70		1.03	9.7	37/43/20						0.147	34.0	38.6	106.6
Ha Tay/Fluvisols	0-20	6.04	2.16	8.9	35/55/10	36	5	9	30	56	0.243	44.2	56.0	112.5
(Cambic Fluvisol)	20-30		1.76								0.226	41.0	53.7	110.3
	30-40		0.59								0.191	30.8	34.2	96.9
	40-50		0.41								0.194	33.1	37.4	107.8
	50-60		0.39								0.198	34.1	36.0	107.9
	60-70		0.33	14.7	45/43/12						0.133	32.2	30.9	104.3
Vinh Phuc/Acrisols	0-20	6.08	0.80	3.2	12/43/45	6[c]	5	11	11	73	0.044	9.1	10.8	44.2
(Haplic Acrisol)	20-30		0.28								0.040	9.1	11.1	36.0
	30-40		0.21								0.024	8.1	10.6	31.4
	40-50		0.21								0.010	6.9	9.7	31.1
	50-60		0.20								0.002	7.2	10.3	28.0
	60-70		0.20	4.89	40/35/25						0.007	7.4	9.9	28.6

[a] Total organic carbon (%); [b] Extracted with 1M NH_4NO_3 1:2.5 soil: solution (sum of Ca, Mg, K and Na, $cmol_c\ kg^{-1}$); [c] % of the particle size fraction (< 2 µm)/(2-20 µm)/(20-200 µm) in soil sieved through 2 mm mesh; [d] % phyllosilicate clay minerals of the bulk soil mineralogy (<2 mm), Vinh Phuc soil contained much quartz in the <2 µm fraction; [e] % of clay mineral in the < 2 µm clay size fraction; [f] Expandable clay is a mixture of highly illitic mixed-layer illite-smectite/illite-vermiculite; [g] Extracted with reverse *aqua regia* ($3HNO_3$:1HCl).

Element balances in peri-urban agricultural systems (Paper I)

Description of input and output flows

Field element balances were calculated for N, P, K, Cu and Zn in vegetable production systems in Bang B (Thanh Tri) and Phuc Ly (Tu Liem) villages in peri-urban areas of Hanoi city. Aquatic vegetables in Bang B received much more irrigation water than dry-land vegetables in Phuc Ly, and the total volume used varied between plots. Biosolids (chicken manure often mixed with ash and rice straw) were applied to Phuc Ly plots at a rate of 17.9-18.4 t ha^{-1} yr^{-1} (fresh weight), while no organic fertiliser was applied to the Bang B plots (Table 10).

The concentrations of N, P, K, Cu and Zn in wastewater used in Bang B were 4.4-28.9, 0.1-4.6, 3-13.5, 0.02-0.23 and 0.02-0.86 mg L^{-1}, respectively, which were significantly higher than in 'natural' river water applied in Phuc Ly. The corresponding concentrations of those elements in irrigation water in Phuc Ly were 0.1-12.7, 0.1-1.9, 1.0-7.5, <0.03 and 0.02-0.24 mg L^{-1} (Paper I). The element concentration in the biosolids applied at Phuc Ly varied strongly throughout the year and between the plots and was in the range 1-14 g N kg^{-1} dw, 1-12 g P kg^{-1} dw and 9-44 g K kg^{-1} dw. The trace metal concentrations in manure were 19-89 mg Cu kg^{-1} dw and 111-290 mg Zn kg^{-1} dw.

Vegetable cultivation was very intensive at both study sites. There were 6-9 crop rotations on the same plot per year. The biomass yields ranged from 110 to 277 ton fw ha^{-1} yr^{-1} (Table 10). Concentrations of Cu and Zn in edible parts of the vegetables ranged from 0.3 to 3.1 and 1.6 to 7.0 mg kg^{-1} fw, respectively, which were below the Vietnamese and FAO/WHO (Cu) safety limits.

Element balances

The field balance calculations showed that the macronutrients N, P and K were present in surplus amounts at all sites. The N surplus was largest for BB2, 882 kg N ha^{-1} yr^{-1} compared with 427, 131 and 85 kg N ha^{-1} yr^{-1} for BB1, PL1 and PL2 respectively (Figure 3). For P and K, the surpluses ranged from 109 to 196 and from 20 to 306 kg ha^{-1} yr^{-1}, respectively. The trace metal balances (Cu, Zn) also showed surpluses. The plots in Phuc Ly (PL1 and PL2) showed an annual surplus for these elements of between 258 and 314 g ha^{-1} for Cu, and 1363 to 1683 g ha^{-1} for Zn. The surplus for BB1 was 176 g Cu ha^{-1} yr^{-1} and 646 Zn g ha^{-1} yr^{-1} compared with 2683 and 7700 g ha^{-1} yr^{-1} for Cu and Zn respectively at BB2.

The estimation of nutrient input flows showed that irrigation water was an important source of nutrients for the Bang B plots, accounting for 21 and 31% respectively of the total measured input of N and K to BB1. At BB2, where the supply of irrigation water was larger, it accounted for 61 and 66% of the total input of N and K, respectively. Irrigation water used at Bang B supplied 226-995; 13-59 and 124-594 kg ha^{-1} yr^{-1} of N, P and K, respectively.

Table 10. *Description of the study plots in Bang B (BB1 and BB2) and Phuc Ly (PL1 and PL2) villages, Hanoi, and quantification of the major input flows (fertiliser and irrigation) and output flow (harvested crop) for a 12-month period*

	BB1	BB2	PL1	PL2
Farmer	Mr. Lan	Mr. Lan	Mrs. Sau	Mr. Dan
Plot area (m^2)	192	408	356	287
Position	N: 20°57.553' E: 105°49.656'	N: 20°57.446' E: 105°49.528'	N: 21°04.053' E: 105°45.102'	N: 21°04.186' E: 105°45.222'
No. of sub-plots[a]			10	7
Sub-plot area (m^2)			32-40	36-45
Vegetable[b]	Aquatic (2)	Aquatic (4)	Terrestrial (6)	Terrestrial (8)
Input flows				
Seedling/seed type[c]	Seedling	Seedling	Seed	Seed
Biosolids (t ha^{-1})[d]			18.4	17.9
Chemical fertilisers	NPK, Urea, P-fert, K-fert	NPK, Urea, P-fert, K-fert	NPK, Urea, P-fert	NPK, Urea, P-fert
Other fertiliser (t ha^{-1})				
Ash	1.5	2.1		1.1
Horn		0.8		
Irrigation water (m^3 ha^{-1})				
Wastewater	13 400	52 700		
Natural river water			7 900	7 800
Output flow				
Number of crops in rotation/harvests [e]	8/8	6/15	6/7	8/9
Biomass[f]	277	256	226±53	110±30

[a] Plot divided into 7 or 10 sub-plots with different planting dates and/or crop species.

[b] Aquatic vegetables grown in permanently flooded plots. Water depth in the field varies from 5 to 60 cm. The number of species is given in brackets.

[c] Inputs through seedlings were quantified, whereas inputs through seeds were not included since they were considered to be of minor importance.

[d] Chicken manure fresh weight, the water content varied from 38-64% (PL1) and 25-70% (PL2).

[e] The first number is the number of crops in a one-year rotation, the second is the number of harvests in the same plot. Some species can have more than one harvest from the same root.

[f] Fresh weight (ton ha^{-1}), dry matter content ranged from 4 to 18%.

In the Phuc Ly plots, the biosolids contributed 12-25, 38-40 and 46-70% of the total annual measured input of N, P and K respectively, whereas the chemical fertilisers contributed 68-82, 58-60 and 15-27% of total annual measured input of N, P and K respectively.

Biosolids played an important role for the nutrient supply in Phuc Ly. They were not only the largest contributor of K, but also of trace metals. There were no significant differences between the mass input of Cu and Zn at the Phuc Ly sites due to similar concentrations and amounts of biosolids being applied. Biosolids contributed 276-358 g Cu ha^{-1} and 1111-1642 g Zn ha^{-1} annually. The largest inflow contribution to Cu and Zn in Bang B was through wastewater.

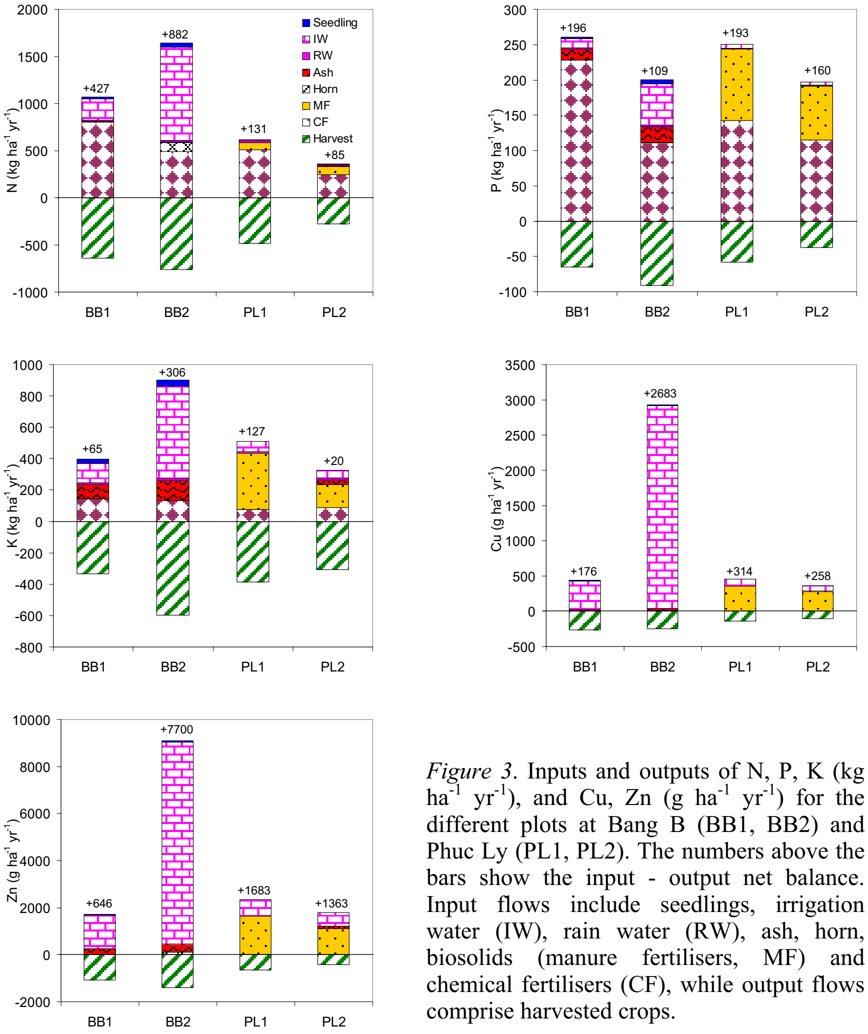

Figure 3. Inputs and outputs of N, P, K (kg ha^{-1} yr^{-1}), and Cu, Zn (g ha^{-1} yr^{-1}) for the different plots at Bang B (BB1, BB2) and Phuc Ly (PL1, PL2). The numbers above the bars show the input - output net balance. Input flows include seedlings, irrigation water (IW), rain water (RW), ash, horn, biosolids (manure fertilisers, MF) and chemical fertilisers (CF), while output flows comprise harvested crops.

Vegetable systems in the two peri-urban areas were intensive in terms of number of crops in rotation, nutrient input and output flows. A comparison with rice-based systems in northern Vietnam (Nguyen, 2003) showed that the amounts of N, P and K applied were 1-4; 3-8 and 2-3 times larger in the vegetable systems compared with the rice systems. The high input levels of nutrients were used to obtain high yields of vegetables.

The agricultural system downstream from Hanoi City received large quantities of elements originating from the inner city because of the influence of wastewater flow, in contrast to the agricultural systems upstream from the city. However, output element flows through crop products were high at both sites due to very intensive peri-urban vegetable farming systems developed to meet the consumption demand in the inner city. The biosolids applied in the peri-urban agriculture of Hanoi city mainly originated from agricultural wastes, while city wastes were only returned to agriculture via wastewater. This pattern is similar to many cities in developing countries (*e.g.* Huang *et al.*, 2006). Hanoi annually discharges approx. 780 000 tons solid waste but only around 6% of that is converted to compost. The rest is dumped in landfill, where the ratio of organic to inorganic material is 1:1 (VEPA, 2005). The amount of wastewater in Hanoi is estimated to be about 460 000 m^3 day^{-1} and this is commonly discharged to rivers without prior treatment. Therefore the amount of biosolids produced in the city is not great (Anh, Barreiro & Parkinson, 2005). There is a high potential for reuse of biosolids in agriculture in the future due to the new legislation requiring that wastewater and solid waste should be treated before released to the environment. Therefore the element flows from city to agricultural systems can come to increase and the accumulation of trace metals in agricultural soils will then risk to increase further, especially in the agricultural systems upstream from the city where no city wastes are recycled at present.

The element balance approach enabled element flows to be compared and provided an estimate of the excess of nutrients and trace metals in agricultural soil systems. However, some output flows (*e.g.* gaseous emissions of N, leaching and surface runoff) and input flows (*e.g.* atmospheric deposition) were not included, leading to underestimation of both output and input flows. For BB2 in particular, where the highest volume of irrigation water was used, there were possibly losses of water-borne nutrients through leaching and surface runoff. Gaseous emissions could be a significant output flow for N. Thus the surpluses indicated elements at risk of losses through leaching, surface runoff or gaseous emissions (N), or soil accumulation (*e.g.* Öborn *et al.*, 2003; Huang *et al.*, 2006).

Effects of using wastewater on soil chemical properties (Paper II)

Soil samples were collected to assess the impacts of sewage irrigation on agricultural soils in peri-urban areas of Hanoi and Nam Dinh city (Paper II). The quality of irrigation water used to irrigate these areas is shown in Table 11. There were significantly higher concentrations of most elements (*i.e.* N_{tot}, P_{tot}, K, Na, Cd, Cu, Pb and Zn) in wastewater compared with river water.

The analyses showed that the soils that had received municipal wastewater for irrigation had significantly higher TOC and N_{tot} contents than the soils irrigated with river water, 0.3-0.8% C and 0.04-0.05% N, respectively. Wastewater-irrigated soils had significantly higher 'total' (Rev *Aq Reg*) concentrations of Cu, Pb and Zn compared with the control soils, 3.5-3.8, 3.2-5.1, and 7.0-8.2 mg kg^{-1}, respectively (Figure 4).

Municipal wastewater contains a variety of inorganic substances from domestic and industrial sources, including a number of potentially toxic elements such as As, Cd, Cr, Cu, Hg, Pb and Zn (Muchuweti *et al.*, 2006). According to the annual report on the environmental status prepared by the Vietnam Environment

Protection Agency (VEPA, 2004), toxic elements are commonly present in the domestic wastewater of many cities. Even if the toxic materials in wastewater are not present in concentrations likely to affect humans or to limit their agricultural use (Table 11), they might be higher than concentrations in natural river water, which would lead to contamination of agricultural soils in the long-term. In this study, the concentrations of trace metals (Cu, Pb and Zn) in the wastewater-irrigated soils were significantly higher than in the control, indicating that the application of wastewater had enriched the soil with trace metals (Figure 4). Liu *et al.* (2005) studied the impact of sewage irrigation on trace metal contamination in Beijing and stressed that metals were enriched in soil due to sewage irrigation. This was also the conclusion in earlier publications regarding the effects of sewage irrigation on soils (Wang, 1998; Al-Ogaily, Al-Harbi & Ali, 1999; Mireles *et al.*, 2004; Mapanda *et al.*, 2005).

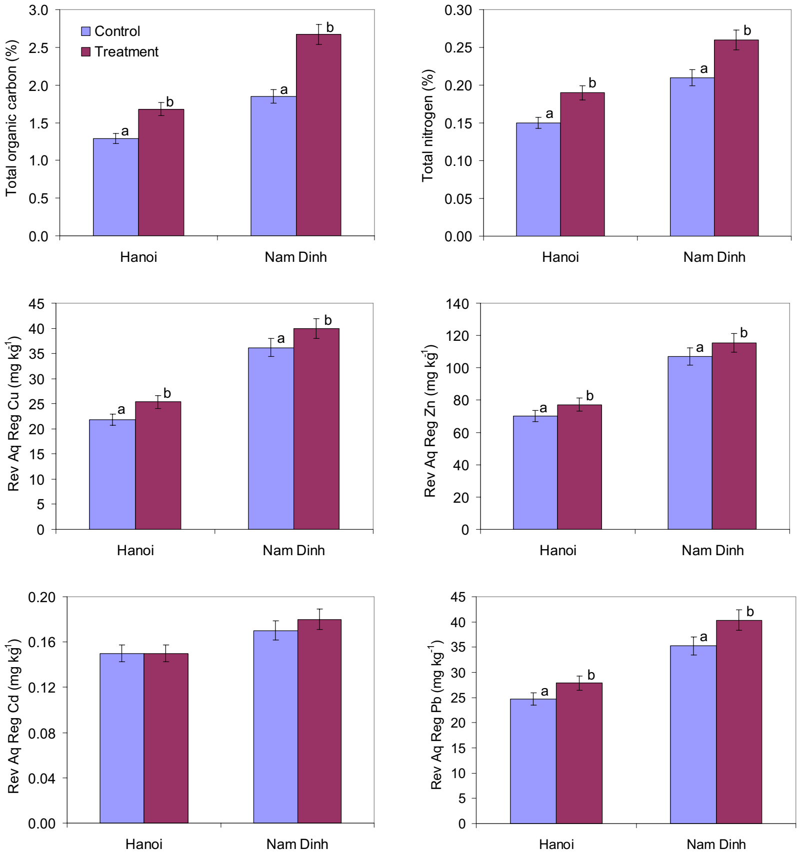

Figure 4. Effect of reuse of wastewater on total organic carbon (%), total nitrogen (%) and reverse *aqua regia* (Rev *Aq Reg*)-extractable Cd, Cu, Pb and Zn (mg kg^{-1}). Different letters indicate significant differences between treatments at the same site ($P<0.05$).

The application of wastewater at two peri-urban sites in Hanoi and Nam Dinh city increased soil pH by approximately 0.3 units in wastewater-irrigated soils compared with non-wastewater irrigated soils (Paper II). Other analyses showed that the pH was significantly higher for wastewater compared with natural river water (Table 11), which might explain the higher pH for wastewater-irrigated soils. In addition, the higher concentration of cations such as Na and K in wastewater contributed to increased EC and exchangeable Na and K in the wastewater-irrigated soils (Paper II). Furthermore, the high pH in wastewater-irrigated soils might have reduced the mobility of trace metals in soil, which probably increased the accumulation of metals.

Table 11. *Water quality of Red River water (RR) and wastewater (WW) used for irrigation in Hanoi and Nam Dinh and Maximum Acceptable Concentrations (MAC_{IR}) for irrigation water of Cd, Pb and Zn ($\mu g\ L^{-1}$) in Vietnam (MOSTE, 2000). The different letters indicate significant differences between sources of water at the same site (P<0.05)*

No.	Parameter	Hanoi (Paper I)		Hanoi (Paper II)		Nam Dinh (Paper II)		MAC_{IR}
		RR (n=25)	WW (n=33)	RR (n=4)	WW (n=6)	RR (n=4)	WW (n=5)	
1	pH			6.9^a	7.9^b	7.1^a	8.0^b	5.5-8.5
2	EC (dS m^{-1})			0.21^a	0.86^b	0.20^a	0.82^b	
3	N_{tot} (mg L^{-1})	3.1^a	17.4^b	3.9^a	19.2^b	4.1^a	10.8^b	
4	P_{tot} (mg L^{-1})	0.8^a	2.3^b	0.5^a	4.4^b	0.6^a	2.0^b	
5	K (mg L^{-1})	4.3^a	8.7^b	4.1^a	12.8^b	3.1^a	6.8^b	
6	Na (mg L^{-1})			28.6^a	135.7^b	32.5^a	85.5^b	
7	Ca (mg L^{-1})			54.6	54.3	46.7	48.9	
8	Mg (mg L^{-1})			14.2	12.4	12.5	10.1	
9	Pb (μg L^{-1})			2^a	3^b	1^a	2^b	100
10	Zn (μg L^{-1})	91^a	385^b	24^a	236^b	32^a	67^b	1000
11	Cu (μg L^{-1})	10^a	82^b	18^a	82^b	14^a	42^b	
12	Cd (μg L^{-1})			0.5^a	0.9^b	0.2^a	0.5^b	10

Effects of using biosolids on soil chemical properties (Paper II)

Use of biosolids as a nutrient source in crop production significantly increased organic carbon and total nitrogen content in the soil (Paper II). Treatment of biosolids involved application of 7-63 t ha^{-1} of composted manure or 10 to 90 t ha^{-1} of chicken manure incorporated into the top 20 cm of the soil. The soil bulk density was 1.2 t m^{-3} for the Ha Tay soil and 1.3 t m^{-3} for the Vinh Phuc soil. Theoretical estimations showed that soil organic carbon would initially have increased by a factor of 3.3×10^{-3} and 5.5×10^{-3} t^{-1} biosolids for Ha Tay and Vinh Phuc, respectively, as a result of the biosolids application. The field experimental data showed that the organic carbon increase for composted manure was in agreement with the calculated value. However, for chicken manure the increase in measured carbon content was lower than the estimate (Table 12). This was probably due to the decomposition of chicken manure that occurred during the experimental period, and that was less pronounced in the composted manure. An increase in TOC and N_{tot} through application of biosolids has also been found in previous studies (White, Loftin & Aguilar, 1997; Illera *et al.*, 2000; Walter *et al.*, 2000). However, there was no significant increase in soil organic matter and total nitrogen in a study by Garrido *et al.* (2005), probably because of the lower rate (4.5 t ha^{-1}) of biosolids applied in that study.

Although biosolids have been demonstrated to be useful nutrient sources for agricultural soils, the beneficial properties of biosolids can, depending on their origin, be limited by their contents of potentially harmful substances. The soil amended with biosolids in the present study had higher 'total' (Rev *Aq Reg*) concentrations of Cu (only for the Vinh Phuc site) and Zn than the control soils. Ogiyama *et al.* (2006) reported Zn accumulation in soils due to animal manure application, while Sloan *et al.* (1997) reported that biosolids application significantly increased total concentrations of Cu and Zn in the soils studied, although the differences were less than the initial increase anticipated for the application of biosolids. This may be due to plant trace metal uptake. Furthermore, the increase in trace metal contents in soil will be dependent on the biosolids application rate (Garrido *et al.*, 2005). In the present study, there was a significant increase in 'total' Zn for application rates greater than 21 t ha^{-1} for composted manure and 30 t ha^{-1} for chicken manure (Paper II).

Table 12. *Effect of biosolids application on TOC, N_{tot} and reverse aqua regia-extractable trace metals. The regression model was y = Intercept + Slope × Biosolids application rate (t ha^{-1})*

	Intercept	Slope × 10^3	R^2	P
Ha Tay				
TOC (%)	2.39	3.38	0.63	0.03
N_{tot} (%)	0.28	0.19	0.84	< 0.001
Cu (mg kg^{-1})	44.1	4.12	<0.01	0.836
Zn (mg kg^{-1})	112.5	13.25	0.58	0.037
Cd (mg kg^{-1})	0.26	0.38	0.23	0.365
Pb (mg kg^{-1})	56	30.30	0.17	0.657
Vinh Phuc				
TOC (%)	0.90	4.33	0.89	< 0.001
N_{tot} (%)	0.12	0.25	0.72	0.002
Cu (mg kg^{-1})	9.48	6.32	0.68	0.007
Zn (mg kg^{-1})	43.77	35.04	0.73	0.001
Cd (mg kg^{-1})	0.03	0.18	0.27	0.301
Pb (mg kg^{-1})	10.2	1.58	0.06	0.573

Although the 'total' concentrations of Cd and Pb in chicken manure and Cd in composted manure were higher than in the experimental soils, the concentrations of Cd and Pb in biosolids-amended soils were not significantly higher, although there was an increasing trend. The concentration of Pb in composted manure was lower than that in experimental soil (Ha Tay). In addition, the short-term nature (one time) of biosolids application in these experiments may have contributed to the lack of a significant effect on these elements.

Trace metals in biosolids are generally strongly sorbed to the biosolids matrix. Thus, trace metals added to soil with biosolids are less phytoavailable than those added as simple inorganic salts (Li *et al.*, 2001). There was no significant effect on the NH_4NO_3-extractable fraction of trace metals compared with the level in control soils (Paper II). However, the potential soluble fraction of Cd, Cu and Zn (EDTA-extractable) was significantly higher than in control soils, but not that of Pb. This indicates that adding biosolids to agricultural soils can increase binding sites or even act as a sink for trace metals already present in soil, reducing metal concentration in the soil solution, despite the biosolids having higher metal concentrations than the soil itself (Mahler, Ryan & Reed, 1987; Hooda & Alloway, 1993). Cripps, Winfree & Reagan (1992) found that application of biosolids at a rate of 11 t ha^{-1} increased availability of Cu in soil, but that neither Cu nor Zn was leached from the surface soil.

Solubility of trace metals in soils (Paper III)

Copper

Dissolved Cu in the batch experiments is shown in Figure 5a. The total dissolved Cu concentration in a background of 0.02 M $NaNO_3$ (1:15 soil:solution ratio without adding acid/base) ranged from 0.1 to 0.2 μM and was a small fraction compared to the EDTA-extractable fraction. The salt solution probably extracts only the soluble and easily exchangeable Cu fraction, whereas Cu complexed to soil organics and oxides is not released (Steinnes, 1984; Ross, 1996).

Soil titrations with acid indicated that dissolved Cu increased strongly with decreasing pH. Dissolved Cu was lowest at pH 5-7 (≤0.3 μM) and then increased with decreasing pH. Figure 5a shows that Cu was much more soluble at pH values lower than 5 than in the range 5-7. At pH higher than 7, the dissolved Cu increased slightly with increasing pH.

The Cu in the Ha Tay soils was much more soluble than in the Nam Dinh and Hanoi soils, followed by the Vinh Phuc soils having the same acid pH value. This was probably due to the EDTA-extractable fraction of Cu in soil being highest for Ha Tay soils, followed by Nam Dinh, Hanoi and Vinh Phuc soils.

Zinc

The total Zn concentrations in the solutions extracted by $NaNO_3$ were lower than 0.4 μM. Figure 5b shows that the solubility of Zn in these soils was strongly pH-dependent, and Zn solubility increased strongly with decreasing pH. However, when pH was increased above 7.5, the solution concentration of Zn had a tendency to increase again (*e.g.* Vinh Phuc).

The effect of pH on metal adsorption and metal solubility has been reported by authors elsewhere (McBride & Blasiak, 1979; Kuo & Baker, 1980; Gustafsson, 2001). This phenomenon was observed in the earlier study by McBride & Blasiak (1979), who reported that Zn retention increased with increasing pH, as is usual for metal cations. However, their work also showed that when pH was increased above 7.5, the solution concentration of Zn increased. This might be due to the dissolution of organic ligands that complex Zn (Kuo & Baker, 1980).

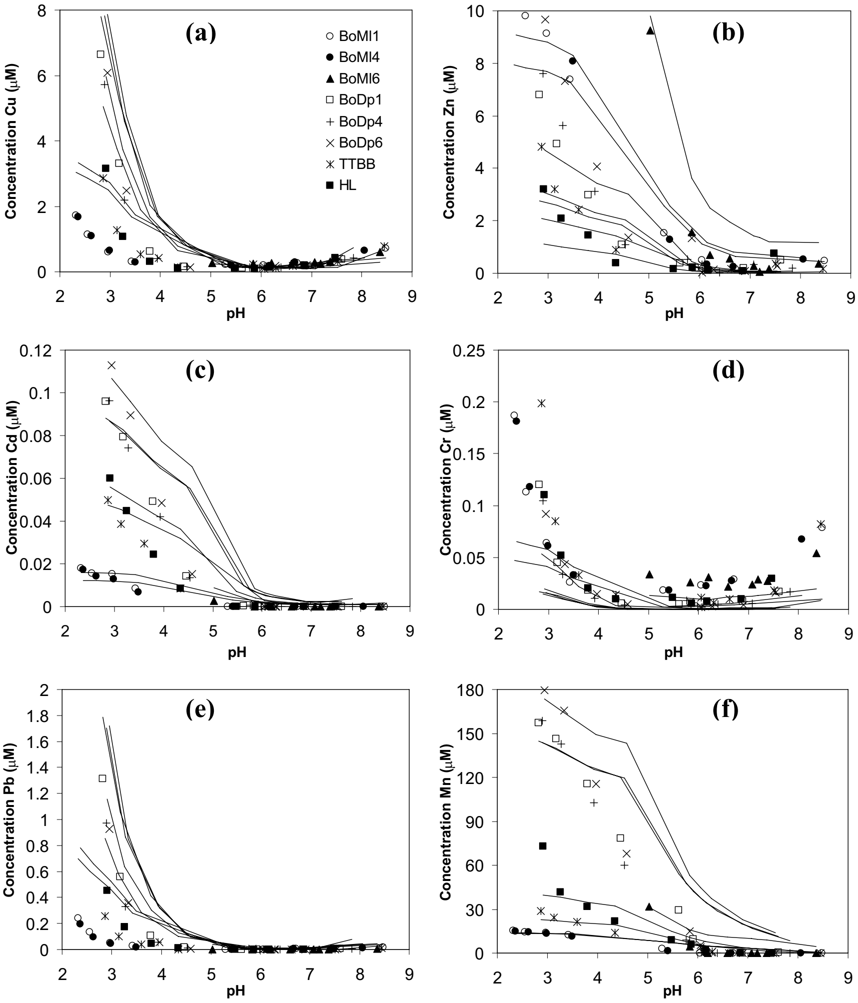

Figure 5. Total dissolved Cu, Zn, Cd, Pb, Mn and Cr(III) as a function of pH for the soils studied; Vinh Phuc (BoMl1, BoMl4, BoMl6), Ha Tay (BoDp1, BoDp4, BoDp6), Hanoi (TTBB) and Nam Dinh (HL). Titrations of soil samples with HNO_3 and NaOH. Ionic strength (I) = 0.02 M (as $NaNO_3$). The observations are shown as points, whereas the model simulations (MS-DSGM) are shown as lines.

The solubility of Zn was possibly dependent on the soil texture and organic matter content. The solubility of Zn in solution was higher for the Acrisols (in Vinh Phuc) than for the other soil (Fluvisols) at the same pH value. This could be explained by the Fluvisols having a higher content of clay particles and organic matter than the Acrisols. Shuman (1975) studied the effect of soil properties on Zn adsorption and found that soils high in clay or organic matter had a higher adsorption capacity for Zn than sandy soils low in organic matter. In addition, the higher EDTA-extractable fraction of Zn in the Acrisols is possibly caused by greater effects of pH on Zn solubility in the Acrisols.

Cadmium

The total Cd concentrations in the solutions extracted by 0.02 M $NaNO_3$ were lower than the detection limit (3.6×10^{-10} M Cd). This was probably due to the fact that the Cd concentrations in these soils (EDTA-extractable fraction) were low and that the salt solution did not release large amounts of adsorbed Cd to the soil solution. The EDTA-extractable concentration of Cd in the Acrisols was very low (0.02-0.05 mg kg^{-1}), while the values for the Fluvisols ranged from 0.1 to 0.24 mg kg^{-1}. Figure 5c shows the concentration of soluble Cd as a function of pH was higher for the Fluvisols than for the Acrisols. As for Cu and Zn, the total Cd concentration in the solution decreased with increasing pH. However, at higher pH values (> 6) the dissolved Cd concentration was smaller than the detection limit for all soils. For the Acrisols, the dissolved Cd increased to above the detection limit when pH was < 5, probably due to the fact that these soils contained a low but measurable EDTA-extractable fraction of Cd. In general, decreased Cd solubility with increasing pH can be explained in terms of increasing negative surface charge (Street, Sabey & Ladsay, 1978).

Lead, manganese and chromium

The results for dissolved Pb in the batch experiments are shown in Figure 5e. The total Pb concentration in the solution extracted by 0.02 M $NaNO_3$ (1:15 soil: solution ratio without acid or base added) was lower than the detection limit (3.6×10^{-8} M Pb).

Normally, dissolved Pb increases strongly with decreasing pH. This is also shown by the results of this study. In the pH range 2.3-5, the Pb release by the Acrisols increased by a factor of 6 to 9 for every unit decrease in pH. For Fluvisols, the Pb release increased by a factor of 8 to 13 for every unit decrease in soil pH (in the pH range 2.8-5).

For Mn, the pH dependence of the total dissolved concentration resembled that of Cd. The increase in concentration of dissolved Mn with increasing acidity of the soil solution was more rapid for Fluvisols, probably due to Fluvisols containing a higher EDTA-extractable fraction of Mn. Therefore adding the same amount of protons caused more Mn to be released to the solution in the soil containing a greater Mn-EDTA fraction. The solubility of Mn was smaller than 5.3 μM at pH values above 6. In this case, the increased adsorption with increasing pH can be explained both by the increased adsorption of Mn^{2+} and by the increased likelihood of MnO_2 precipitation following Mn oxidation.

For Cr, the total dissolved concentration was lowest between pH 4.5 and 7. The Acrisols (Vinh Phuc) had a higher dissolved Cr concentration than the Fluvisols (Ha Tay) when pH was higher than 5. At pH values lower than 4, dissolved Cr increased rapidly with decreasing pH and was not greatly different between the Acrisols and Fluvisols.

Modelling of metal binding (Paper III)

The curves in Figure 5 show that prediction of dissolved metals as a function of pH using MS-DSGM gave a similar trend to measured metal concentrations as a function of pH. Figure 6 shows the relationship between measured metal concentration in the soil solution and the concentration predicted using MS-DSGM and MS-DNGM from batch experiments. The model simulations for Zn in most cases agreed rather well with the observations. The overall RMSE value was 0.49 for MS-DSGM and 0.55 for MS-DNGM (Table 13). For Cu too, the simulations in most cases corresponded rather well with measured data for all soils. The overall RMSE values were 0.36 and 0.29 for MS-DSGM and MS-DNGM, respectively. The model results showed that the proportion of Cu bound to SOM accounted for the highest proportion of sorbed Cu (86-98%, Table 13 and Figure 7). The predominance of SOM as a Cu sorbent across the pH range investigated is in agreement with both earlier observations and modelling results (McGrath, Sanders & Shalaby, 1988; Wang *et al.*, 2001; Dijkstra, Meeussen & Comans, 2004). For Zn, SOM is a significant sorbent, but at high pH the model results suggest that adsorption of Zn on HFO should also be considered (Figure 7).

Table 13. *Goodness-of-fit for the MS-DSGM and MS-DNGM models and proportion of metal sorption on different adsorbents*

	n[a]	MS-DSGM				MS-DNGM			
		RMSE[b]	SOM[c]	HFO[c]	Clay[c]	RMSE[b]	SOM[c]	HFO[c]	Clay[c]
Cu	69	0.36	86(45-99)	6(0-19)	8(0-55)	0.29	98(81-100)	1(0-5)	1(0-19)
Zn	66	0.49	50(10-89)	16(0-70)	33(0-90)	0.55	74(18-98)	7(0-65)	19(0-82)
Cd	31	0.38	67(15-96)	7(0-43)	26(0-85)	0.20	92(54-100)	<1(0-3)	8(0-46)
Pb	40	0.75	46(5-93)	51(0-95)	3(0-26)	0.65	54(5-95)	42(0-95)	4(0-41)
Mn	69	1.34	42(6-80)	11(0-92)	47(2-91)	1.04	70(27-96)	5(0-48)	25(1-73)
Cr	67	1.28	49(5-99)	29(0-75)	22(0-95)	1.56	100	-	-

[a] Number of observations above the detection limit.

[b] Root mean square error (RMSE) of simulated and observed logarithms of total dissolved concentrations.

[c] Fractional (%) metal adsorption on soil organic matter (SOM), iron (hydro)oxide. (HFO) and clay as mean (min-max) (see Figure 7).

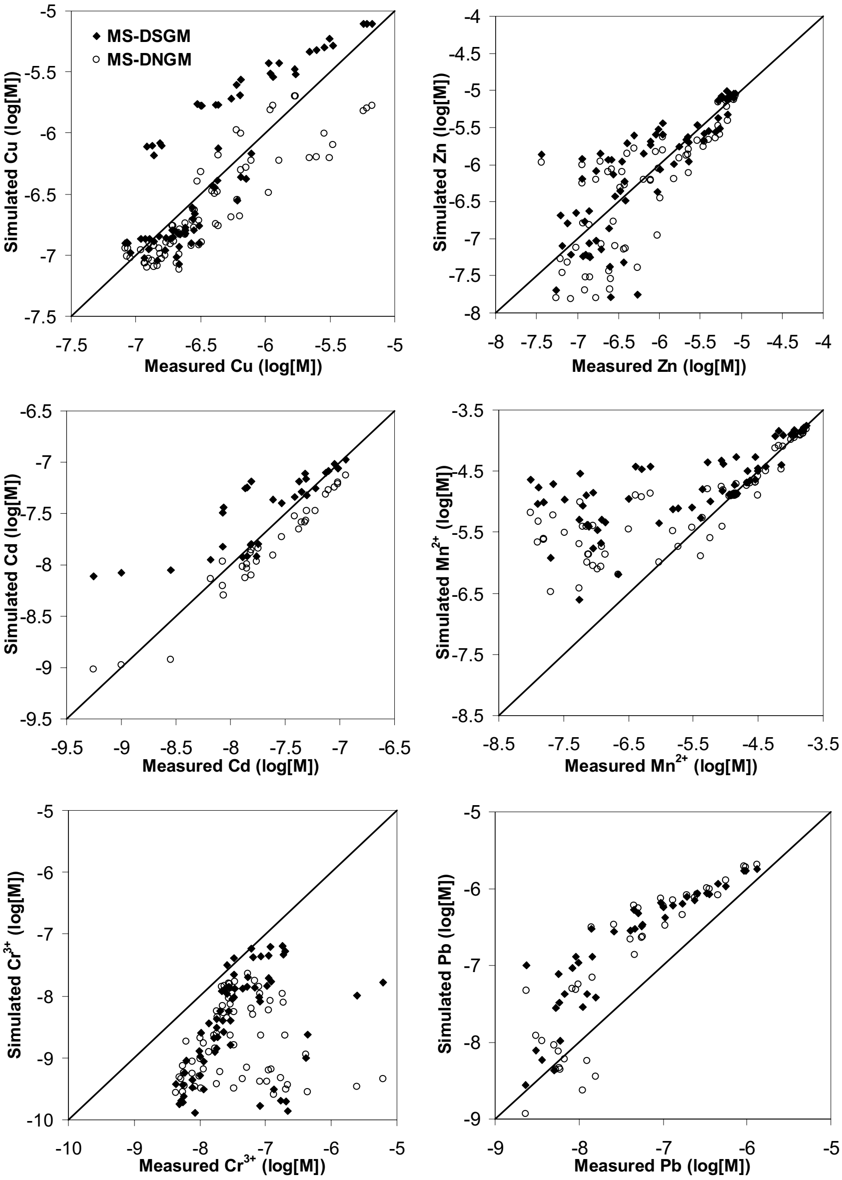

Figure 6. Comparison of the simulated values of $\log[\mathrm{Cu}]_{\mathrm{tot}}$, $\log[\mathrm{Zn}]_{\mathrm{tot}}$, $\log[\mathrm{Cd}]_{\mathrm{tot}}$ $\log[\mathrm{Pb}]_{\mathrm{tot}}$, $\log[\mathrm{Cr}]_{\mathrm{tot}}$, and $\log[\mathrm{Mn}]_{\mathrm{tot}}$ with measured values. The line indicates the perfect 1:1 fit.

The model fits for Cd were very good for all soils. The overall RMSE for Cd was 0.38 for MS-DSGM and was slightly improved to 0.20 when simulated by MS-DNGM. The results indicated that the Cd binding was determined mainly by complexation to organic matter. Dissolved Mn was not satisfactorily simulated, either with MS-DSGM or with MS-DNGM (RMSE = 1.34 and 1.04, respectively). In most cases, both the MS-DSGM and the MS-DNGM prediction overestimated

Mn, especially in the high pH range, possibly due to Mn oxidation and formation of MnO_2 under these conditions not being considered in the models.

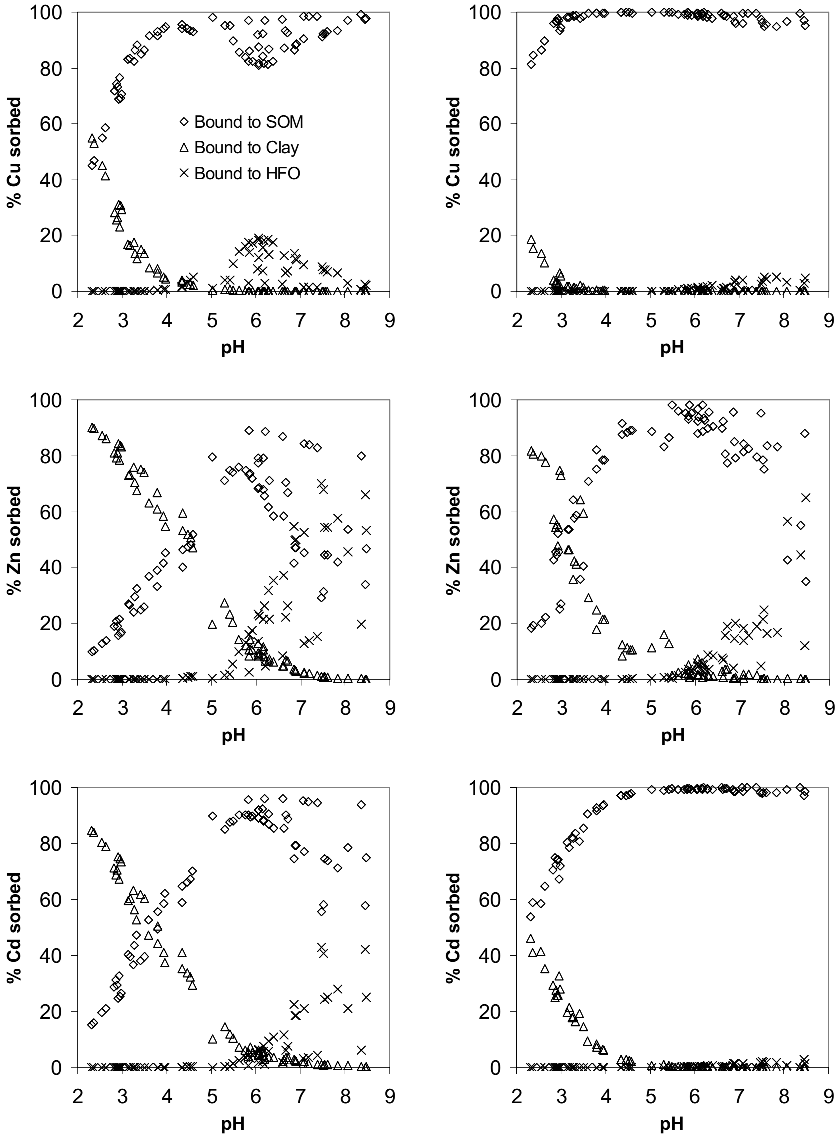

Figure 7. Adsorption (as percentage of total sorbed) of Cu, Zn and Cd on soil organic matter (SOM), clay and hydrous ferric oxide (HFO). Left panes are the MS-DSGM predictions, while right panes are the MS-DNGM predictions.

The value of total dissolved Cr(III) predicted by the model in most cases agreed poorly with the observed total dissolved concentration of Cr, with both MS-DSGM and MS-DNGM underestimating the dissolved Cr(III) concentration. One possible reason may be uncertain complexation constants; for example the surface complexation constant for HFO suggested by Dzombak & Morel (1990) is only an estimate based on a linear free-energy relationship. Alternatively, the poor model fit can be explained by poor efficiency of the EDTA solution in removing Cr(III) from oxides and organic matter.

For Pb, both models often overestimated dissolved Pb. The RMSE value for the MS-DSGM fit was 0.75. The RMSE was slightly improved to 0.65 when simulated by MS-DNGM. The models showed that Pb is relatively strongly bound to Fe oxides at pH > 4. One reason for the poor fit could be that Pb is even more strongly bound to Fe and Mn oxides than the models suggest. The importance of Mn oxides has been stressed previously (McKenzie, 1980). In our case, we did not include Mn oxides in the model. In addition, XRPD data (Paper III) indicate that a variety of different crystalline Fe oxides are present in the samples so a more complex parameterisation would have been more beneficial. Another possibility is that the models underestimate Pb binding to organic matter. The finding that Pb binding to soil is underestimated with generic model parameters for metal-humic complexation is in agreement with previous studies (Weng *et al.*, 2002; MacDonald & Hendershot, 2006; Linde, Öborn & Gustafsson, 2007).

Environmental risk assessment

Element balance approach

One way to illustrate the long-term sustainability of a system is to relate the flows and balances to the existing nutrient or metal soil pool, and assess the accumulation/depletion rate (Öborn *et al.*, 2003). For the sites examined in this study, the surplus of P and K was 109-196 and 20-306 kg ha^{-1} yr^{-1}, respectively. In 100 years time this will lead to an increase in the soil storage of between 10 and 19 t ha^{-1} for P and between 2 and 30 t ha^{-1} for K (Table 14). In these calculations, losses by leaching and surface run-off were not taken into account. The high surplus of N, P and K can be related to changes in soil fertility, or the potential risk of losses to the wider environment. The latter may cause eutrophication (N and P) of surface waters or contamination of groundwater (Huang *et al.*, 2006).

Trace metal accumulation in the soil may have harmful effects on soil biota and result in accumulation in the human food chain (Giller, Witter & McGrath, 1999; Singh & Kumar, 2006). At present, the concentrations of Cu and Zn in the soils at the two study sites do not exceed Vietnamese MAC values (Table 14). The time to reach the MAC was roughly estimated for the surface soil layer (0-20 cm), assuming a surplus similar to that at present. The annual change in the existing soil pool was estimated to be 0.3-4.6 and 0.4-4.5% yr^{-1} for Cu and Zn, respectively. The calculated time to reach the MAC was only 21 (Cu) and 38 (Zn) years for the heavily wastewater-irrigated site (BB2), whereas it was longer (156 to 229 years) at the sites where chicken manure was the main metal input source (PL1 and PL2), indicating a risk of harmful long-term effects if the present input rates of metals remain or increase even further.

Table 14. *Total P, K (g kg^{-1}) and 'total' (Rev Aq Reg) Cu and Zn (mg kg^{-1}) soil concentrations, soil pools (0-20 cm) (P, K kg ha^{-1}; Cu, Zn g ha^{-1}), balance (input-output, P, K kg ha^{-1} yr^{-1}; Cu, Zn g ha^{-1}yr^{-1}), estimated annual change in the soil pool (%), annual change in soil concentration (P, K g kg^{-1}; Cu, Zn mg kg^{-1}), and years to reach the maximum allowable concentrations (MAC)*

	System	Element			
		P	K	Cu	Zn
Soil concentration	Bang B	1.07	7.97	25.20	74.00
	Phuc Ly	1.01	8.41	30.70	76.80
Soil pool^{a}	Bang B	2 456	18 362	58 086	170 570
	Phuc Ly	2 552	21 288	77 671	194 304
Balance (surplus)					
BB1	Bang B	196	65	176	646
BB2	Bang B	109	306	2683	7700
PL1	Phuc Ly	193	127	314	1683
PL2	Phuc Ly	160	20	258	1363
% Change in soil pool^{b}					
BB1	Bang B	8.0	0.4	0.3	0.4
BB2	Bang B	4.4	1.7	4.6	4.5
PL1	Phuc Ly	7.6	0.6	0.4	0.9
PL2	Phuc Ly	6.3	0.1	0.3	0.7
Annual change in concentration					
BB1	Bang B	+0.09	+0.03	+0.08	+0.28
BB2	Bang B	+0.05	+0.13	+1.16	+3.34
PL1	Phuc Ly	+0.08	+0.05	+0.12	+0.67
PL2	Phuc Ly	+0.06	+0.01	+0.10	+0.54
Years to reach MAC^{c}					
BB1	Bang B			325	450
BB2	Bang B			21	38
PL1	Phuc Ly			156	185
PL2	Phuc Ly			189	229
Permitted metal load (g ha^{-1} yr^{-1})^{d}					
Germany				1300	2500
Sweden (by sewage sludge)				300	600
EU, directive 86/278EEC				12000	30000
EU proposed long-term limits				1800	4500

[a] Dry bulk density of the soil was 1.15 and 1.27 g dm^{-3} at Bang B and Phuc Ly, respectively.

[b] Annual change in the soil pool calculated as surplus/soil pool (0-20 cm)×100.

[c] Maximum allowable concentrations (MAC, 50 Cu mg kg^{-1}, 200 mg Zn kg^{-1}) for Vietnamese agricultural soils.

[d] According to Landner & Reuther (2004).

However, the calculation did not take into account input flows such as atmospheric deposition, or output flows such as leaching and surface runoff, *i.e.* both inputs and outputs were underestimated. If both leaching and surface runoff were quantified and included in the balance calculations the time to reach the MAC of trace metals would actually be longer, but the losses would pose a potential threat to surface water and groundwater quality. However, most probably the atmospheric deposition is higher that the losses through surface run-off and leaching, as has been demonstrated in previous studies in agricultural soils (Andersson, 1992; Bengtsson *et al.*, 2006). If atmospheric deposition were to be included and assumed to be similar to data reported by Wong *et al.* (2003) for Guangzhou, China (60-225 g Cu ha^{-1} yr^{-1} and 387-847 g Zn ha^{-1} yr^{-1}), the calculated time to reach MAC would decrease. Thus a surplus of trace metals will accumulate in the soil and impair the quality of the soil and that of the surrounding environment, *e.g.* through increased uptake in crop products and losses to water bodies through leaching and surface runoff.

Modelling approach

The modelling approach was used to simulate possible future scenarios. It was based on the assumption that in the long-term, application of wastewater and biosolids to agricultural soils together with other land use practices would lead to a change in soil conditions, *e.g.* concerning 'total' metal concentrations, soil pH and soil organic matter content. Four scenarios (A-D) were developed and one of the multisurface models (MS-DNGM) was used to predict the dissolved metal concentrations (Cd, Cu and Zn) in the soil solution for risk assessments including the present Vietnamese MAC for Cd (2 mg kg^{-1}), Cu (50 mg kg^{-1}) and Zn (200 mg kg^{-1}) (Table 8). Figure 8 shows predicted dissolved Cd for scenario A, B, C in Fluvisols and Acrisols.

In scenario A, the predicted dissolved Cd increased with increasing 'total' metal concentration up to MAC (2 mg Cd kg^{-1}). Dissolved Cd ranged between <0.001 and 0.01 mg L^{-1} for Fluvisols (Figure 8a). For Acrisols, dissolved Cd ranged between 0.001-0.05 and the water quality standard was exceeded long before MAC was reached (at about 0.7 mg Cd kg^{-1}, assuming 50% of total Cd to be potentially soluble) (Figure 8b). Dissolved Cu and Zn ranged between 0.07-0.23 and 0.02-0.65 mg L^{-1} respectively for Fluvisols. The corresponding values for Acrisols ranged between 0.14-1.43 and 0.26-11.1 mg L^{-1} (Paper IV). In scenario B, the model predicted that the dissolved metal concentrations were non-linearly related to SOM. Dissolved metal concentrations increased sharply when SOM was changed to below the average level recorded for the soil type, *i.e.* below 4% in Fluvisols and 2% in Acrisols. At low SOM and high Cd content (*e.g.* when SOM <1.8% and Cd_{tot} = 1.5 mg kg^{-1} for Fluvisols and SOM <2% and Cd_{tot} = 0.8 mg Cd kg^{-1} for Acrisols) the water quality standard was exceeded by dissolved Cd (Figure 8c-d).

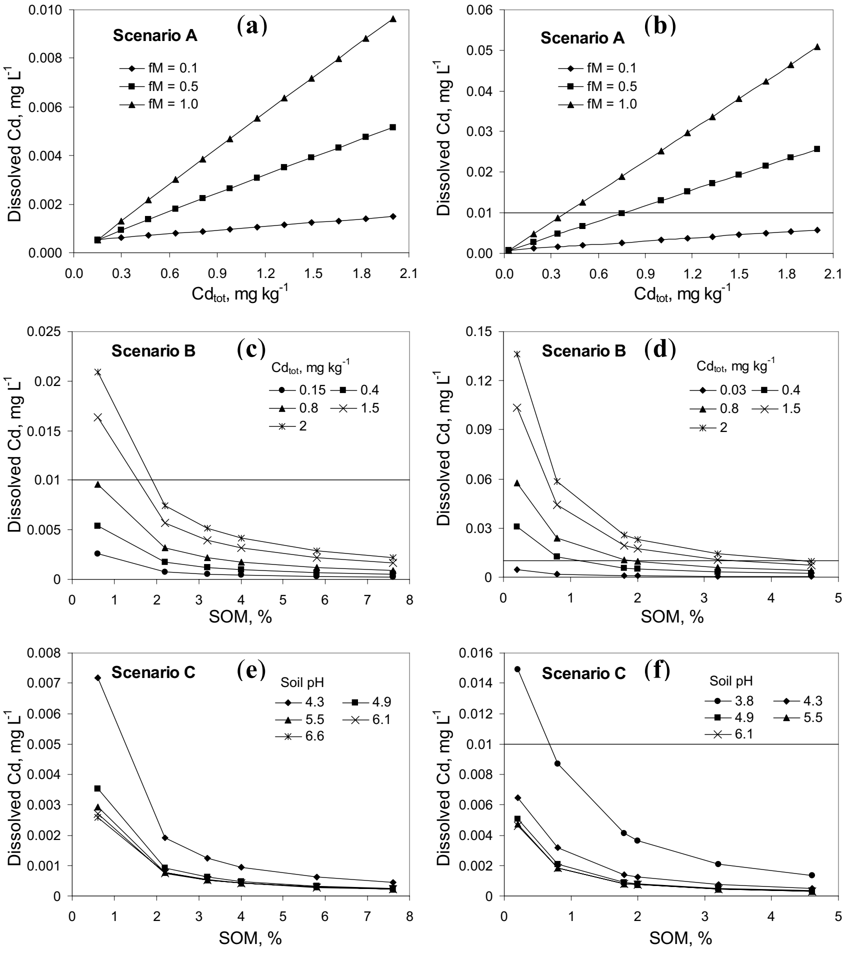

Figure 8. Prediction of dissolved Cd of Fluvisols (left panes) and Acrisols (right panes) with different scenarios (A, B, C). The horizontal lines are maximum acceptable concentration of Cd in groundwater and irrigation water (0.01 mg Cd L^{-1}). The f_M was assumed to be 0.5 in scenario B and obtained by EDTA extraction in scenario C.

In scenario C, the dissolved metal concentrations for Fluvisols were predicted to be lower than 0.01 mg Cd L^{-1} (Figure 8e), 0.45 mg Cu L^{-1} and 0.2 mg Zn L^{-1} (Paper IV) when soil pH was 4.3 and SOM was 0.6%. For Acrisols the dissolved metal concentrations were predicted to be higher, 0.014 mg Cd L^{-1} (Figure 8f), 1.2 mg Cu L^{-1} and 3.5 mg Zn L^{-1} (Paper IV) when soil pH was 3.8 and SOM was 0.2%. The difference between scenarios C and D was in the setting of 'total' metal concentration. Total concentrations of Cd, Cu and Zn in scenario *C* were set at present soil concentrations (Table 8), whereas they were set at Vietnamese MAC in scenario D. Thus, the predicted dissolved metal concentrations were much higher in scenario D, especially in Acrisols, where dissolved Cd, Cu and Zn were up to 0.67, 8.5 and 50 mg L^{-1}, respectively (Figure 9).

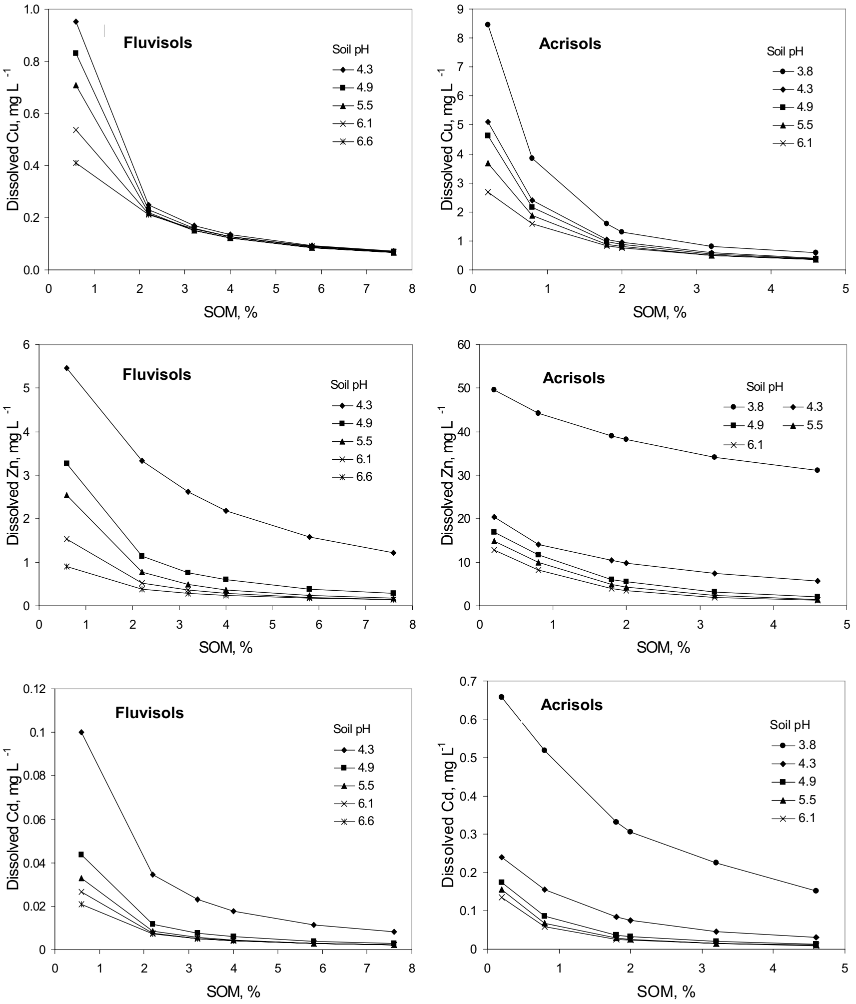

Figure 9. Prediction of dissolved Cu, Zn, and Cd as a function of soil organic matter (SOM) at different soil pH values. The f_M was assumed to be 0.5 and the total concentration of trace metals was assumed to be at MAC (*Scenario* D).

The model simulations indicated that in Acrisols, the Vietnamese MAC for agricultural soils are too high to ensure that soluble metal concentrations remain below the critical quality standards for groundwater (0.01 mg Cd L^{-1}, 1.0 mg Cu L^{-1}, and 5.0 mg Zn L^{-1}) or irrigation water (0.01 mg Cd L^{-1} and 1.0 mg Zn L^{-1}) (Paper IV). In Fluvisols, the MAC for Cu and Zn seem to be at reasonable levels from a water protection point of view, with the exception of soils with very low SOM or pH. In the short term, application of organic waste and wastewater will increase the SOM and also the total trace metal concentrations (and often also the pH), leading to a limited increase in soluble metal concentrations. However, in the long-term, decomposition of SOM and soil acidification might be expected and that will lead to a release of these metals, which may affect the quality of agricultural products as well as soil quality and ecosystem health. Long-term application of metal-contaminated organic waste and wastewater to soils might also affect groundwater and surface water quality. At current soil metal concentrations and soil conditions, the study soils are at no risk, but since Acrisols are approaching the current Vietnamese MAC they will probably exceed the water quality standards, especially for Cd but also for Zn. These results indicate the potential risk of Cd and Zn leaching from Acrisols to groundwater and surface waters, as well as transfer to food products by plant uptake (Datta & Young, 2005).

Possible pathways of trace metal movement after loading to agricultural soils are incorporation into the soil, uptake by plants, leaching and surface runoff. Modelling different scenarios allowed the proportion of the metals in a mobile and possibly bioavailable form in the soils to be predicted and the risk of metal losses to be assessed. However, the limitations of these assumptions were that we did not include the time factor, *e.g.* decomposition of organic matter and change in soil pH over time. In addition, the plant uptake and losses of metals through leaching and runoff were not included in the model. Furthermore, scenarios B and D assumed that only 50% (f_M=0.5) of metal loadings were in potentially soluble form. If this fraction were to increase, the dissolved metal concentration in the soil solution would show a corresponding increase (*e.g.* scenario A). The next step could be to include hydrological modelling and plant uptake to give a more reliable description of long-term trace metal behaviour in the soil environment.

Conclusions and recommendations

Intensive vegetable cultivation in peri-urban agriculture in Vietnam implies high nutrient flows and high nutrient surpluses. In the present study, the surplus for N ranged from 85 to 882 kg ha^{-1} yr^{-1}, compared to 109-196 and 20-306 kg ha^{-1} yr^{-1} for P and K respectively. The Cu and Zn surplus ranged from 0.2-2.7 and 0.6-7.7 kg ha^{-1} yr^{-1} respectively, indicating a high risk of accumulation in soil and associated dissemination through the food chain. The high surplus of N, P and K creates a potential risk of losses to the wider environment, causing eutrophication (N and P) of surface water or contamination of groundwater.

There are high element (nutrient) flows through agricultural products from peri-urban areas toward urban areas, but the element flows returning to peri-urban areas through waste recycling differ between downstream and upstream areas of cities. Wastewater from the inner city is a major nutrient source for intensive peri-urban agriculture in downstream areas. In intensive peri-urban agriculture in upstream areas, where there is no opportunity to receive wastewater from the city, the main nutrient source is biosolids in the form of animal manure (mixed with straw and/or ash) produced by other villages specialising in animal production. Hence there is no nutrient recycling from urban areas. In addition, chemical fertilisers are used in both areas.

Application of wastewater and biosolids in agriculture can directly supply nutrients and improve a number of soil properties. The field experiments indicated that wastewater-irrigated soils or soils into which biosolids were incorporated had elevated concentrations of total organic carbon and total nitrogen. Soil pH and exchangeable base cation concentrations are also elevated in wastewater-irrigated soils due to the alkaline nature of wastewater.

At present, the ‘total’ (reverse *aqua regia*-extractable) concentrations of Cd, Cu, Pb and Zn in soils receiving wastewater or biosolids do not exceed Vietnamese MAC, but accumulation of some of these trace metals was observed, posing a potential risk in the future. The ‘total’ concentration of Cu, Pb and Zn in the wastewater-irrigated soils was significantly higher than that in the control soils, and there was a significant increase in total concentrations of Zn in biosolids-treated soils. In addition to trace metals, other potentially hazardous substances, not included in this study, could be present in the wastes.

The modelling study of metal binding indicated that soil organic matter is a major sorbent for Cd, Cu, and Zn in tropical Acrisols and Fluvisols. Multi-surface models including the soil sorption surfaces, *i.e.* iron hydroxides, organic matter and phyllosilicate clay, provided good model fits for the total dissolved concentrations of Cd, Cu and Zn in all soils studied. Regarding Cr(III), Mn and Pb, however, modelling was not successful and further refinements of the models will be required. pH is the main factor controlling the solubility of metals in these soils. In addition, the adsorption of Cd and Zn on phyllosilicate clays becomes more important at pH values below 3.5, while at pH values above 7 the adsorption of those trace metals on iron hydroxides should be considered. The success of the models for Cd, Cu and Zn indicates that MS models can be used for simulation of the binding and release of these metals in tropical surface soils subjected to additions of biosolids and wastewater.

As indicated, soil organic matter is the major soil component controlling the solubility/sorption of trace metals in tropical soils with relatively low organic matter contents. Therefore any change in soil organic matter will lead to changes in the concentrations of metals in the soil solution. The scenario simulations showed that in the short-term, application of organic waste and wastewater increases soil organic matter content as well as the total metal concentrations (and often the pH values as well), leading to a limited increase in soluble metal concentrations. However, decomposition of soil organic matter is rapid in subtropical/tropical climates and that might lead to release of adsorbed metals. In addition, processes resulting in soil acidification will also increase trace metal solubility. Hence increased trace metal loads may in the long-term affect the quality of agricultural products, as well as soil, water and whole ecosystem functions.

The current Vietnamese MAC values for agricultural soil are set at 50 mg Cu kg^{-1}, 200 mg Zn kg^{-1} and 2 mg Cd kg^{-1}. These MAC values are probably too high for Acrisols, especially for Cd, to ensure soluble metal concentrations below the current quality standards for groundwater and irrigation water. For Cd, there might also be a risk for too high concentrations in food crops.

Some recommendations

There is some concern regarding the large surplus of nutrients currently applied to intensively managed peri-urban agricultural soils. The accumulation of trace metals was considerable in the peri-urban agricultural system studied in this thesis and was primarily attributable to use of contaminated urban wastewater. To prevent potential risks to the environment, a twofold approach is required, namely: (1) Treatment of urban waste prior to discharge; and (2) options to improve nutrient management, including the development of strategies that would benefit the profitability of farming systems whilst also reducing the size of annual nutrient surpluses, thus helping to reduce the risk of further environmental damage.

This study also indicates that long-term application of metal-contaminated organic waste and wastewater to soils might lead to high concentrations of dissolved metals that can jeopardise not only the soil quality but also the quality of groundwater and surface water, or lead to enhanced metal concentrations in food crops. With the soil metal concentrations and soil conditions prevailing in Vietnamese soils at present, the studied soils are at no risk, but if these soils gradually approach the current Vietnamese MAC values, the dissolved metal concentrations in Acrisols will most probably exceed the water quality standards, especially for Cd but also for Zn and Cu. These results indicate the potential risk of leaching of Cd, Cu and Zn from Acrisols to groundwater and surface water, as well as transfer to food products by plant uptake. In Acrisols, the MAC for Cd in soil should be set at 0.5 mg kg^{-1} or lower, in order to guarantee water quality standards. The MAC for Zn and Cu might also need to be revised for acid soils low in organic matter.

Soil organic matter and soil pH are the main factors controlling the solubility of trace metals in the soil environment. However, it should be noted that the decomposition of soil organic matter in tropical areas usually occurs much more rapidly than in other regions. In the short-term, an improvement of the soil organic matter content gives rise to more adsorption of trace metals in the soil and limits their mobility. This suggests that improving soil organic matter content and controlling soil pH can help to limit an increase in dissolved metal concentration in the soil solution and reduce the risk of leaching to groundwater and to the environment.

Paddy rice soils in Vietnam are generally switched from flooded to non-flooded conditions. One question that can be raised is if the timing of flooded conditions affects the metal solubility/sorption and uptake in plants. Further research, including experimental, laboratory and modelling work, is needed in order to develop a better understanding of the trace metal dynamics in soil-plant systems with alternating reducing and oxidizing conditions.

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