SUSTAINABLE MANAGEMENT OF HEAVY METALS

IN AGRO-ECOSYSTEMS

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SUSTAINABLE MANAGEMENT OF HEAVY METALS

IN AGRO-ECOSYSTEMS

S.W. Moolenaar

Proefschrift

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NWO

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Stellingen

1. Men zou minder stelling moeten nemen en meer echt in gesprek moeten gaan.

2. Het tegelijkertijd "in balans brengen" van de zware metalen cadmium, koper, lood en zink in de Nederlandse landbouw is een vrijwel onmogelijke opgave.
   [naar: G.L. Velthof, P.J. van Erp, S.W. Moolenaar. 1996. Optimizing fertilizer plans of arable farming systems. II. Effects of fertilizer choice on inputs of heavy metals. *Meststoffen* 1996: 74-80; Dit proefschrift]

3. Indien men inzicht wil krijgen in de ophoping van zware metalen in cultuurgrond, nopen de grote verschillen tussen en binnen landbouwsystemen tot een specifieke analyse op bedrijfsschaal.
   [Dit proefschrift]

4. "Gemengde bedrijfsvoering" op regionale schaal biedt goede perspectieven voor verbetering van de kwaliteit van het landelijk gebied.

5. In geval van bepaalde toedieningen aan de bodem, zoals GFT-compost, is het nodig de veranderingen in bodemsamenstelling mede in beschouwing te nemen om de resulterende zware-metalenaccumulatie op veldschaal meer realistisch te kunnen berekenen.
   [Dit proefschrift]

6. Het toekennen van het predikaat "ecologisch" aan wijn op basis van het niet gebruiken van organische pesticiden in wijngaarden, is net zo zot als toekenning van dit predikaat zou zijn aan vlees afkomstig van de intensieve varkenshouderij waar men de ammoniak-uitstoot minimaliseert.

7. Dynamische zware-metalenbalansen vormen een geschikte basis om duurzaamheidsindicatoren af te leiden die aangeven welk metaal op welk moment en in welk milieu-compartiment tot problemen kan leiden.
   [Dit proefschrift]

8. Bodembescherming is meer gebaat bij normen die betrekking hebben op de belasting van de bodem met verontreinigende stoffen dan bij bodemkwaliteitseisen die aangeven in welke toestand de bodem dient te verkeren.
   [Th.M. Lexmond, S.E.A.T.M. van der Zee, M.G. Keizer, F.A.M. de Haan. 1997. Wet bodembescherming: De kwaliteit van een beleidsinstrument. *BODEM* 1: 26-29]

9. Analyse van milieu-effecten op basis van zware-metalenbalansen is gebaat bij incorporatie van de speciatie en competitie van zware metalen in de bodem.
   [Dit proefschrift]

10. De ontwikkeling van "duurzame landbouw" moet niet plaatsvinden op basis van een blauwdruk, maar is wel gebaat bij het ontwerp van een proefdruk.

11. "In het kader van actief bodembeheer kan juist aandacht gegeven worden aan het dynamische karakter van "duurzame ontwikkeling" door (veranderend) bodemgebruik en bodemkwaliteit zodanig op elkaar af te stemmen dat de gebruikswaarde van de bodem op termijn gehandhaafd blijft of toeneemt. "Multifunctionaliteit" is dan richtinggevend voor een proces waarin zorg voor en verbetering van de kwaliteit van de bodem een centrale plaats krijgen."

    [Technische commissie bodembescherming (TCB). 1996. *Tenslotte: verzamelde slotbeschouwingen.* Negentienhonderdvijfennegentig]

12. In het onderzoeksgebied van Industrieel Metabolisme en Industriële Ecologie moet men voor ogen houden dat de natuur a-moreel is en dus ook niet als "wetgever" dan wel "leermeester" op kan treden ten aanzien van de inrichting van de maatschappij en de toelaatbaarheid van menselijke behoeften. Wel is het zinnig om de principes uit de ecologie (hoe werkt het?) te betrekken op de vragen uit de ethiek (wat is goed?) teneinde een gezonde grondslag voor duurzame ontwikkeling te leggen.

    [naar: M. Korthals. 1994. Duurzaamheid en democratie. Inaugurele rede, Landbouwuniversiteit; C.B. DeWitt. 1992. Ethics, Ecosystems and Enterprise. Discovering the meaning of food security and development. *In*: K. Smith & T. Yamamori (Eds.). *Growing our future: Food security and the Environment.* Kumarian Press Inc., West Hartford; C.B. DeWitt. 1995. Ecology and ethics: relation of religious belief to ecological practice in the Biblical tradition. *Biodiversity and Conservation* 4: 838-848]

13. De interdisciplinaire meerwaarde van een onderzoeksprogramma mag niet verwacht worden van het inzetten van AIO's dan wel OIO's.

14. Wetenschap zonder godsdienst is lam; godsdienst zonder wetenschap is blind.

    [Einstein]

15. De waarheidsaanspraken van de evolutieleer zijn natuurwetenschappelijk niet te bewijzen. Het debat over schepping versus evolutie wint dan ook aan duidelijkheid als men ronduit zou erkennen dat men zich baseert op geloofs-vooronderstellingen.

16. Lichte slapers hebben een zwaar leven.

17. Close-harmony zingen is helend voor de ziel.

    [n.a.v. het tijdperk van 'the Singing Soul Brothers']

18. De relatie mens-akker is fundamenteel, maar de relatie mens-God is beslissend.

    [n.a.v. *De Bijbel*: Genesis]

Stellingen behorend bij het proefschrift 'Sustainable Management *of* Heavy Metals *in* Agro-ecosystems', Simon W. Moolenaar, Wageningen, 11 mei 1998.

Abstract

Moolenaar, S.W., 1998. **Sustainable management of heavy metals in agro-ecosystems**. Doctoral Thesis, Wageningen Agricultural University, Wageningen, The Netherlands. 191 pages.

Sustainable management of heavy metals in agro-ecosystems necessitates an analysis of heavy-metal fluxes, resulting accumulation in soil and associated risks. In order to determine the options for a sustainable heavy-metal management in agriculture, balance sheets are used as a means to quantify input and output flows in agro-ecosystems and to calculate resulting heavy-metal accumulation in soil. In this thesis, heavy-metal management of agro-ecosystems is studied within the context of 'substance flow analysis'. Heavy-metal balance studies on different spatial scales are presented. The (im)possibilities to aggregate results on the field scale to higher levels of analysis are explored and different approaches to assessing heavy-metal balances (*i.e.*, top-down and bottom-up) are compared. The 'dynamic soil composition balance' approach is introduced. This new approach takes into account the composition of both soil amendments and soil when calculating heavy-metal accumulation in soil. Cadmium, copper, lead, and zinc flows of arable, dairy and mixed farming systems are studied and the most viable options for a sustainable heavy-metal management are discussed. Measurements at an experimental farm in the Cremona district (Italy) are used to make projections of the long-term development of heavy-metal contents in soil, crop removal and leaching at different application rates of sewage sludge and Bordeaux mixture. Effects of different land use change scenarios on copper speciation and consequent copper mobility are studied by incorporating a well defined speciation model into a dynamic copper balance. 'Sustainability indicators' are introduced that can be used to assess the effects of current agricultural practices and of different management options that aim at preventing quality standards from being exceeded. Literature and measurements with regard to long-term field experiments are interpreted and the options for calculating realistic dynamic heavy-metal balances of soil are discussed in the research context of this thesis. To enhance sustainable management of heavy metals in agro-ecosystems, further development is recommended with respect to scale aspects, environmental management systems, economic and environmental indicators, dynamic modeling, and monitoring. Furthermore, a coherent EU policy and the development of an ethical foundation are needed to advance sustainable agriculture.

Keywords: accumulation, agro-ecosystems, arable farming, balance (sheet), cadmium, copper, dairy farming, environmental management system, heavy-metal, indicator, industrial ecology, land use change, lead, mixed farming, (dissolved) organic matter, soil amendment, soil pollution and protection, substance flow analysis, sustainability, vineyard, zinc.

Aan Anneke

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Simon Moolenaar

Wageningen, februari 1998

CONTENTS

The contents of this thesis are based on the following self-contained papers:

Chapters 2-4. Moolenaar, S.W. & Th.M. Lexmond. Balancing heavy metals:
I. General aspects of heavy-metal balance studies in agro-ecosystems.
II. Heavy-metal balances and -management in European agro-ecosystems.
III. Heavy-metal balances of agro-ecosystems on the field scale.
(submitted).

Chapter 5. Moolenaar, S.W., Th.M. Lexmond & S.E.A.T.M. van der Zee. 1997. Calculating heavy-metal accumulation in soil: A comparison of methods illustrated by a case-study on compost application.
Agriculture, Ecosystems and Environment 66: 71-82.

Chapter 6. Moolenaar, S.W. & Th.M. Lexmond. 1998. Heavy-metal balances of different agro-ecosystems in the Netherlands.
Netherlands Journal of Agricultural Science (in press).

Chapter 7. Moolenaar, S.W. & P. Beltrami. 1998. Heavy-metal balances of an Italian soil as affected by sewage sludge and Bordeaux mixture applications.
Journal of Environmental Quality 27 (4) (in press).

Chapter 8. Moolenaar, S.W., E.J.M. Temminghoff & F.A.M. de Haan. 1998. Dynamic copper balances of contaminated sandy soil as affected by changing soil organic matter content and pH.
Environmental Pollution (in press).

Chapter 9. Moolenaar, S.W., S.E.A.T.M. van der Zee & Th.M. Lexmond. 1997. Indicators of the sustainability of heavy-metal management in agro-ecosystems.
The Science of the Total Environment 201: 155-169.

Chapter 10. Moolenaar, S.W. & Th.M. Lexmond. Requirements for calculating heavy-metal balances of soil.
(submitted).

CHAPTER 1

GENERAL INTRODUCTION

The research project

In 1993, the Netherlands Organization for Scientific Research (NWO) launched a priority research program on 'Sustainability and Environmental Quality'. Within this program, a METALS sub-program focusses on the accumulation of metals in the economy and the environment, the mechanisms behind these processes, the associated risks, the possibilities for a sustainable management of metal flows, and their consequences for society and environment.
The METALS program studies cadmium, copper, lead, zinc, and aluminum. Criteria for the selection of these metals were that they are related to environmental problems, they are extensively used in economic processes (resulting in diffuse emissions into the environment), they have accumulative properties, and the metals as a group have a wide range of (toxico-)chemical and economic characteristics. The METALS research program consists of five projects:
1. Development of a general materials balance model
(Institute for Environmental Studies; Free University of Amsterdam);
2. Economic modeling of materials-product chains for chain management
(Faculty of Economics and Econometrics; Free University of Amsterdam);
3. Possibilities for linking economic and substance flow models
(Centre of Environmental Science; Leiden University);
4. Flows and accumulations of non-ferro metals in the building sector
(Department of Environmental Science; University of Amsterdam);
5. Heavy-metal fluxes and accumulation in agriculture
(Department of Environmental Sciences; Wageningen Agricultural University).

Accumulation in economic/environmental cycles is thus studied in detail for two sectors of the economy *i.e.*, the building sector (4) and the agricultural sector (5).
This Ph.D. thesis has resulted from the research on sustainable heavy-metal management of agro-ecosystems in the Netherlands and some other European countries (project 5).

The 'heavy metals'

Definition
The classic definition of a metal refers almost exclusively to physical properties of the elemental state (*e.g.*, ductility, electrical conductivity). Some commonly accepted functionally descriptive terms to classify metals in bio-environmental studies are 'trace metal', 'micro-nutrient' and 'heavy metal'.
A trace metal may be defined as a metal found at concentrations of less than 0.1% (*i.e.*, <1000 mg kg^{-1}) in soil (Jenkins & Gareth Wyn Jones, 1980). Sometimes this term is also used for elements which are required in small quantities by specified (groups of) organisms. More recently, the term micro-nutrient is used to describe this second meaning (Phipps, 1981). The term heavy metal is now often used to

mean any metal with atomic number >20. Also, a definition based on density (*i.e.*, > 5-6 g cm^{-3}) is used (Davies, 1980).
Phipps (1981) disqualified the use of the term heavy metal for the purpose of describing metal behavior in biological systems and he stated that it is a 'hopelessly imprecise, thoroughly objectionable and extremely misleading' term. As an alternative to functional descriptions of metals it is possible to revert to a purely chemical classification which must be related to bio-environmental processes such as uptake selectivity, functional role, or toxicity pattern. Because the interaction (complex formation) of metals with living systems is dominated by the behavior of metal ions as electron acceptors, the categorisation of metal ions in terms of differential 'Lewis acidity' has become accepted. In the original scheme, metal ions were described as class *a*, class *b* or borderline. The class *a* ions ('hard-acids') preferentially form complexes with similar non-polarisable ligands (particularly oxygen donors), and the bonding in these complexes is mainly ionic. Conversely, the class *b* ions ('soft-acids') preferentially bind to polarisable ligands to give rather more covalent bonding.
In this thesis, the metals cadmium (Cd), copper (Cu), lead (Pb), and zinc (Zn) and their ionic forms will together be called 'heavy metals', because this term, although imprecise, is commonly used in literature and provides a useful umbrella term for metals classed as environmental pollutants (cf. Tiller, 1989).

Properties and toxicity
Metals are naturally circulated by biogeochemical cycling through the biosphere, lithosphere, hydrosphere, and atmosphere. Metallic elements are found in all living organisms, where they play a variety of roles. They may be structural elements, stabilizers of biological structures, components of control mechanisms, and enzyme activators or components of redox systems. Therefore, some metals are essential elements and their deficiency results in impairment of biological functions. When present in excess, essential metals may also become toxic. Other metals are not known to have any essential function and they may give rise to toxic manifestations even when intakes are only moderately in excess of the 'natural' intake (Friberg & Nordberg, 1986). Unlike the majority of organic chemicals that can be eliminated from tissues by metabolic degradation, the metals as elements are indestructible and therefore have the potential for accumulation. The only way metals can be eliminated from tissue is by excretion. Accumulation in tissue does not necessarily imply the occurrence of toxic effect since inactive complexes or storage depots are formed in the case of certain metals. (Clarkson, 1986).

<u>Cadmium:</u>
Geochemically, Cd is a rare element. It is not found in pure state in the natural environment and its concentration in common rock forming minerals is low. The indigenous Cd content of much of the world's agricultural land seldom exceeds a few mg kg^{-1}. The natural source of Cd in the soil is through weathering of Cd-

containing parent material and rocks. Introduction of Cd into the economic system and consequently in the environment mainly occurs unintentionally by the mining and use of (Cu, Zn, phosphate and iron) ores.
Cadmium occurs naturally with Zn and Pb in sulfide ores. It is mainly obtained as a by-product from the refining of Zn. Although Cd has been recognized as an element for only a relatively short time (since 1817), environmental pollution has taken place for several thousand years, ever since man started to produce metals from ores which happened to contain Cd.
Because Cd and Zn have some similarities, Cd is able to mimic the behavior of the essential element Zn in its uptake and metabolic functions. Unlike Zn, however, Cd has not been associated with any biological function and it has been shown to be toxic both to plants and animals. The presence of Cd disturbs enzyme activity, probably due to the much higher affinity of Cd for thiol groupings (SH) in enzymes and other proteins. In animal nutrition Cd is a cumulative poison; it is mainly stored in the kidneys and to some extent also in the liver and spleen. The primary reason for its differential accumulation is the presence of a specific metal-binding protein called metallothionein. This protein binds Cd and other metals like Zn and Cu. The presence of this protein in organs like liver and kidney, and its induction by exposure of animals to high amounts of the metals that it binds, are responsible for the high levels of Cd found in these organs. Excess Cd results in damage to the kidney tubules (where it affects reabsorption functions of the proximal tubuli resulting in a relatively large increase in the excretion of low molecular-weight proteins *i.e.*, tubular proteinuria), rhinitis (inflammation of the mucous membrane of the nose), emphysema (a chronic disease of the lungs in which the alveoli become excessively distended) as well as other chronic disorders. In marked contrast to Pb, Cd does not induce neurological disorders (Sharma, 1980; Friberg *et al.*, 1986).
Dietary intake constitutes the major source of long-term low-level body accumulation of Cd. The Cd content in plants may be raised and thus become hazardous to man. Cadmium differs from Pb in that it can be transported readily from the soil via the plant root to the upper plant parts (Mengel & Kirkby, 1982). Cadmium transfer from soils to the edible parts of agricultural food crops is significantly greater than for other heavy metals (except Zn). The detrimental impact of Cd becomes apparent only after decades of continuous exposure. Although acute Cd toxicity caused by food consumption is rare, chronic exposure to high Cd levels in food could significantly increase the accumulation of Cd in kidneys. Since the detrimental effect of low-level Cd exposure takes a long time to develop, treshold levels defining maximum safe dietary intake of Cd are difficult to establish. The harmful effects associated with a particular Cd intake level may be magnified or lessened by interacting elements (like Zn, Cu) present in the diet (Page *et al.*, 1981).

Copper:

Copper is one of the few metallic elements to occur in a pure metal state in the earth's crust. It has been exploited by man since 5000 BC, and has, together with

iron, been termed one of the cornerstones of civilization. The ready formation of organo-copper complexes is of great significance. This affinity for organic materials is reflected in the essentiality of Cu for all forms of life. The main biological role of Cu is as a constituent, normally in the prosthetic group, of oxydizing enzymes (*e.g.* ascorbic acid oxidase and cytochrome oxidase) which are important in oxidation-reduction processes. So, both Cu deficiency and excess are of consequence for the integrity of biochemical functions in living organisms. Copper deficiency may bring about an iron-deficiency-type of anemia. Excessive intake of Cu has been shown to cause a variety of toxic effects in animal experiments (Aaseth & Norseth, 1986). Sheep are particularly susceptible to Cu toxicosis. Copper poisoning has been reported in sheep under natural grazing conditions in some parts of Australia, where Cu-bearing parent rocks have resulted in high Cu contents in soils and plants. Molybdenum is a potent antagonist of Cu metabolism in ruminants and low molybdenum intake promotes hepatic accumulation of Cu (Bremner, 1979).
The most apparent morphological effects of Cu deficiency in plants are related to (reduced or non-existent) lignification. A decrease in lignification occurs even with mild Cu deficiency and is thus a suitable indicator of the Cu nutritional status of a plant. Copper deficiency affects grain, seed, and fruit formation much more than vegetative growth due to the nonviability of the pollen of Cu-deficient plants. Copper toxicity in plants is generally manifested as chlorosis and stunting of growth. The chlorotic condition may result from iron deficiency and the extent of Cu-induced iron chlorosis may be affected by climatic and soil conditions not connected with Cu toxicity. Crop stunting due to Cu excess can arise from a combination of factors, including antagonism with other nutrients and reduced root growth and penetration into the soil. The basic deleterious effect of Cu on growth is related to the root system (Lepp, 1981; Lexmond & Van der Vorm, 1981).
The impact of Cu deficiency on agriculture depresses potential food production in many parts of the world. At the same time, the continued use of Cu in (agro-) industrial processes generates increasing quantities of contaminated by-products (Lepp, 1981). The main concerns about Cu toxicity in agriculture are the long-term use of Cu-containing fungicides, industrial and urban activities (air pollution, sewage sludge), and the application of pig and poultry slurries. The activity which produces the highest concentrations of Cu in agricultural soils is the use of Cu-containing fungicidal sprays which reach the soil surface directly or indirectly as leaf litter. A 1-2% solution of Cu sulfate, neutralized with hydrated lime and known as Bordeaux mixture, is widely used as a fungicidal spray to prevent mildew on grape vines. Copper is frequently added to the diet of pigs and poultry to achieve improvements in rates of food conversion and growth (Tiller & Merry, 1981).

Lead:

Lead is a very persistent pollutant in the environment and there is no evidence that Pb is essential for either man or animals. Instead, Pb is highly toxic to many organisms under certain conditions. There are few reports of Pb-induced toxic

effects on plants grown in natural ecosystems that have been severely impacted with Pb. The general lack of Pb effects is due to nearly irreversible binding of Pb to soil exchange surfaces and to extracellular root surfaces. Probably, most Pb taken up by plant roots is quickly inactivated through deposition in the roots. The more significant role of plants with Pb in the ecosystem resides in food chain situations where Pb deposited on leaf surfaces may be ingested by herbivores (ranging from insects to horses) grazing these plants (Koeppe, 1981).
Lead is toxic because it mimics many aspects of the metabolic behavior of calcium and Pb inhibits many enzyme systems. In man, one of the chief concerns of Pb toxicity is its effect in causing brain damage particularly to the young. Some chronic effects are related with the hematopoietic system (anemia), the nervous system (encephalopathy), the gastrointestinal tract (stomach complaints etc.), and the kidney (renal tubular dysfunction) (Tsuchiya, 1986).

Zinc:

The Romans already mixed a Zn ore with Cu to obtain brass. By the end of the 19th century Zn began to be produced on a large scale (Elinder, 1986). In many parts of the world Zn deficiency in (economically important) crops is a common phenomenon. At the same time, many of man's activities are increasing Zn levels in the environment to toxic levels (Collins, 1981).
Zinc acts as a catalytic or structural component in numerous enzymes involved in energy metabolism and in transcription and translation. Zinc deficiency symptoms in humans and animals are failure to eat, severe growth depression, skin lesions and sexual immaturity.
Higher plants absorb Zn as a divalent cation, which acts either as a metal component of enzymes or as a functional, structural, or regulatory cofactor of a large number of enzymes. The zinc-phosphorous antagonism is one of the best known nutrient interactions in soil chemistry and plant nutrition (Kiekens, 1995). An inadequate supply of Zn results in chlorosis (in the interveinal areas of the leaf) and stunted growth, with a drastic reduction in yield. One of the first processes influenced by Zn deficiency is RNA metabolism. There is a rapid decrease in RNA levels and the number of ribosomes, which leads to a decrease in the level of normal protein. Common factors that induce Zn deficiency are low soluble Zn, high rainfall, calcareous soils, low soil organic matter, low soil temperatures, etc. The general symptom of Zn toxicity is a retardation of growth, plants being stunted and chlorotic. Zinc has also been shown to alter membrane permeability, which could be one of the primary mechanisms of Zn toxicity (Collins, 1981).
Most of the concern about excessive Zn concentrations in soils relates to its possible uptake by crops and consequent adverse effects on the crops themselves. Together with Cu, Zn is primarily phytotoxic, so the concern about this metal is mainly directed at effects on crop yields and soil productivity. Together with Cd, Zn may be considered as a mobile and bioavailable metal which may accumulate in crops and human diets (Kiekens, 1995).

Soil quality

Soil has many functions in supporting life on earth. Some important functions are the ecological functioning (habitat and protective medium for flora and fauna and contribution to global element cycling), the bearing function (playground and building), the biomass production function (natural vegetation and crop production function), the filtering (or buffer) function (attenuation and degradation of environmental hazardous compounds thus mediating the quality of the air and water resources interfacing with soil), serving as a source for raw-materials (mining and construction) and for archaeological and paleontological research. Soil quality influences the quality of groundwater, which may serve as a resource for drinking water or as surface water recharge (De Haan, 1996a; Blum, 1990; Harris *et al.*, 1996).

Because soil quality is related to the fitness for land use, every type of land use (*i.e.*, soil function) corresponds with different quality requirements (Bouma & Droogers, 1997) and, vice versa, changes in soil quality will impact land use possibilities. Soil may be viewed as a natural resource because it is essential for production of food and fibre and for ecosystem functioning. Degradation of soil shows that soil is also a finite resource that needs sustainable management. Harris *et al.* (1996) define soil quality and health as the fitness of a soil body, within site-specific (*i.e.*, specified land use, landscape and climate) boundaries, to protect water and air quality, to sustain plant and animal productivity and quality, and to promote human health.

If the content of essential heavy metals (Cu, Zn) in soil is low, the supply to organisms will be inadequate and symptoms of deficiency (*e.g.*, growth and yield reduction in the case of crops) may become manifest. In the deficiency range, a positive effect will result from increasing the soil content above the lower critical value as may be done by fertilizer additions. As the supply of the essential metals increases beyond this lower critical content, a level is reached where further increase does not have any effect *e.g.*, on yield. This zone of luxury consumption is the optimal range. Increasing soil content beyond a certain upper critical content, induces adverse effects on soil biota (fauna and flora) and hence on biological activity (toxicity range).

The buffering capacity of soil with respect to soil contamination may be defined as its capacity to delay any (negative) effects of sustained additions of a contaminant because of inactivation. Inactivation is mainly achieved by effective bonding onto soil constituents or sometimes conversion into insoluble compounds. Beyond the upper critical content, soil is considered to be polluted as the buffering capacity is exceeded. The buffering capacity varies widely for different compounds and for different soils and reflects the soil's vulnerability (De Haan, 1996a).

The distinction between soil pollution and soil contamination reflects only a difference in degree of damage to the soil system. Any addition to soil of contaminants can be defined as soil contamination. Due to the soil's buffering capacity, it usually takes some time before negative effects of the contaminant's presence become apparent. Once this situation occurs the soil can be considered as polluted *i.e.*, malfunctioning of the soil is apparent due to an abundant presence or availability of compounds (De Haan, 1996a). Since both essential (Cu and Zn) and non-essential (Cd and Pb) metals become toxic when critical contents are exceeded, excessive metal input to agro-ecosystems can be considered as a stress that potentially affects diversity, productivity and overall functioning of agro-ecosystems (Ross, 1994).

Generally, two types of soil contamination are distinguished *i.e.*, non-point and point source contamination. Non-point source contamination may be defined as a large-scale contamination caused by a particular source or a combination of different sources. Examples are the use of fertilizers and sewage sludge in agriculture and heavy-metal pollution of soil following emissions to air by industrial activities and by traffic. Due to the extended areas involved, possibilities for control and clean-up are very limited. This necessitates protection measures that aim at preventing such diffuse contamination and pollution. Point source contamination is caused by a single and easy to define source, like local pollution by accidental, incidental or deliberate human activities. Here, we are concerned with diffuse (*i.e.*, non-point source) contamination of agricultural soils by heavy metals.

Sources of heavy-metal inputs to (agricultural) soil

Heavy metals enter the economy mainly because of their functional qualities and they are thus found in a wide range of applications for all aspects of daily life. Concern about the entry of various heavy metals into the environment and hence into the human food chain was expressed in an alarming way by Nriagu. In several papers he drew attention to actual and potential problems due to dispersal of metals in the 'total environment' (soil, water, air). Nriagu (1988) described the long-term exposure of mankind to elevated environmental levels of metals as an 'experiment in which one billion human guinea pigs are being exposed to undue insults of toxic metals'.

The natural biogeochemical cycle of heavy metals is caused by wind-borne soil particles, sea-salt spray, volcanoes, forest fires, and biogenic sources. Main anthropogenic sources of heavy-metal emission are metalliferous mining and smelting, incineration plants, automobile exhausts, and fossil fuel combustion. Nriagu (1979) estimated that anthropogenic emissions of heavy metals into the atmosphere appreciably exceed natural emissions of Cd, Cu, Pb and Zn. He suggested that industrial emissions of Pb, Cd and Zn exceed the flux from natural sources by factors of 18, 5 and 3 respectively (Nriagu, 1989). Since most of the metal produced by industrial discharges may be expected to be wasted in the terrestrial biosphere it is expected that the redistribution of such massive amounts of metals at the earth's surface will have a great impact on the global cycles of many elements (Nriagu, 1979). Nriagu & Pacyna (1988) stated that the man-induced mobilization of heavy metals into the biosphere greatly increased circulation of toxic metals through soil, water and air. Transfer to the human food chain is an important environmental issue because metals are non-degradable and the continuing build-up of such toxins in life-support systems entails (partly unknown) ecosystem and health risks.

Because of the volume of their emission, their toxicity and their persistency, a number of policy measures have been drafted in both national and international fora in order to reduce potential ecological and human health risks caused by too high concentrations of heavy metals in environmental media and agricultural produce. Such measures have been succesful with respect to a reduction of industrial emissions to water and air. This might indicate that heavy metals pose no environmental problems anymore. However, overall rates of primary production of metals have not decreased but rather increased for most metals. This implies an accumulation in the economy by increasing amounts of metals in capital goods, intermediate products and/or accumulation in cycles through recycling processes. Consumption-related emissions to air, water and soil may well increase in the future as a result of this accumulation (Guinée *et al.*, 1998).

Most heavy-metal inputs to agricultural soils originate from atmospheric deposition and from different soil amendments (sewage sludge, commercial phosphate, potassium, and nitrogen fertilizers, liming materials, pesticides, manures, compost). According to Anonymous (1997), the Dutch reference values for Cd, Cu, Pb, and Zn are exceeded in about 10, 12, 5, and 10% of the agricultural soils, respectively.

Van Drecht *et al.* (1996) carried out a study to determine current heavy-metal loads on soil in the Netherlands distinguishing soil type, soil use and fertilization practices per crop and deposition patterns. They estimated the percentual contribution of the main input sources of heavy metals to agricultural soils (Table 1.1).

Table 1.1. Percentual contribution of heavy-metal input sources to agricultural soils.

Source	Cd	Cu	Pb	Zn
Animal manure	30	88	17	73
Mineral fertilizer	55	3	8	14
Atmospheric deposition	13	3	71	5
Other	2	6	4	8

Clearly, the main sources are animal manure (Cu and Zn), mineral fertilizer (Cd), and deposition (Pb).

Ter Meulen Smidt & Van Duijvenbooden (1997) estimated the current (1989) and expected (2000) heavy-metal input (ton yr^{-1}) to agricultural soils and calculated the percentual contribution of atmospheric deposition for both years. The expected decrease of total input (Table 1.2) is due to less deposition (Cd, Pb) and due to the use of less and cleaner mineral fertilizer (Cd) and animal manure (Cu, Zn) in the future. Most of the atmospheric deposition originates from neighbouring countries (Cd: 90%, Cu: 60%, Pb: 70%, Zn: 70%) at the moment.

Table 1.2. Current (1989) and expected (2000) heavy-metal input (ton yr^{-1}) to agricultural soils and the percentual contribution of atmospheric deposition for both years.

	1989: input	deposition	deposition	2000: input	deposition	deposition
Cd	13.6	1.7	13%	7.6	1.6	21%
Cu	776	23	3%	676	23	3%
Pb	326	231	71%	137	59	43%
Zn	1829	86	5%	1058	70	7%

Relatively high Cd concentrations are found in rock phosphates used for the manufacture of P-fertilizers. However, Cd concentrations in P-fertilizers can vary widely depending on the origin of the phosphorite raw material with concentrations of Cd in rock phosphate of volcanic origin being low as compared with those of sedimentary origin.

'The potential environmental hazard of fertilizers or other soil amendments depends on the amounts used, the elemental composition of the material, the fraction of constituent elements that are released, the mobility and toxicity of the released elements in the environment, and the ease of incorporation of toxic elements into the biota. The total elemental composition of a material can give a preliminary view of its potential for environmental contamination, and when composition and quantity applied are both taken into account, an estimate of the maximum possible pollution caused through the use of the material can be determined' (Raven & Loeppert, 1996). For typical ranges of heavy metals in agricultural amendments we refer to Alloway (1990), Kabata-Pendias & Pendias (1992), Ross (1994), Driessen & Roos (1996), and Raven & Loeppert (1996).

Aim and contents of this thesis

Sustainable heavy-metal management in agro-ecosystems necessitates an analysis of heavy-metal fluxes, resulting accumulation in soil and associated risks. In order to determine the options for a sustainable heavy-metal management in agriculture, balance sheets are used as a means to quantify input and output flows in agro-ecosystems and to calculate resulting accumulation in soil.

In this Ph.D. thesis, the main research focus is on the cycling and the resulting accumulation of heavy metals in agro-ecosystems. Driving forces which are determined by population, economy, technology and resources are not discussed in depth. Chapters 2-10 are based on papers that have been published in or submitted to international scientific journals. They are compiled in this thesis with slight modifications.

In Chapter 2, general and theoretical aspects of heavy-metal balance studies in agro-ecosystems are described within the broader context of 'substance flow analysis' and 'industrial ecology'.

In Chapter 3, heavy-metal balance studies on different spatial scales in the Netherlands and several other European countries are presented in order to discover the

possibilities for an effective heavy-metal management of agro-ecosystems.
In Chapter 4, the information that is needed to calculate heavy-metal balance sheets on the field scale of agro-ecosystems is discussed. Moreover, the (im)possibilities to aggregate results on the field scale to higher levels of analysis are explored and different approaches to assessing heavy-metal balances (*i.e.*, top-down and bottom-up) are compared.
Chapter 5 provides a detailed picture of the 'dynamic soil composition balance' approach which takes into account the composition of both soil amendments and soil when calculating heavy-metal accumulation in soil.
In Chapter 6, Cd, Cu, Pb, and Zn flows of arable, dairy and mixed farming systems in the Netherlands are studied based on literature data and measurements carried out on experimental farms. After determining the characteristic metal flows of farm-gate and field-scale balances, the most viable options for a sustainable heavy-metal management are discussed.
In Chapter 7, measurements at an experimental farm in the Cremona district (Italy) are used to make projections of the long-term development of heavy-metal (Cd, Cu, Zn) contents in soil, crop removal and leaching at different application rates of sewage sludge and Bordeaux mixture.
Changing land use from arable farming to forestry results in increasing soil organic matter content and decreasing pH. Effects of different land use change scenarios on Cu speciation and consequent Cu mobility are discussed in Chapter 8.
In Chapter 9, 'sustainability indices' are introduced. These characteristic numbers can be used as indicators for potentially adverse effects of current agricultural practices. They can also be used to assess the effects of different management options that aim at preventing quality standards from being exceeded.
In Chapter 10, literature is reviewed with regard to long-term field experiments. Measurements at long-term (organic matter) field trials are interpreted and the options for calculating realistic dynamic heavy-metal balances of soil are discussed in the research context of this thesis.
Finally, the conclusions and recommendations that result from Chapters 2-10 are described in Chapter 11.

CHAPTER 2

BALANCING HEAVY METALS. I.
GENERAL ASPECTS OF HEAVY-METAL BALANCE STUDIES IN AGRO-ECOSYSTEMS

Abstract

Sustainable heavy-metal management in agriculture requires an analysis of heavy-metal fluxes, resulting accumulation and associated risks. This (systems) analysis can be carried out by calculating heavy-metal balance sheets, which characterize different agro-ecosystems as to their heavy-metal input, output, and accumulation. In this chapter, general aspects of heavy-metal balance studies in agro-ecosystems are described within the broader context of substance flow analysis and industrial ecology.

Introduction

To define strategies that ensure a sustainable Cd, Cu, Pb, and Zn management of agro-ecosystems, an analysis of the fluxes of these heavy metals in agriculture, their accumulation in agricultural soils, and associated risks, should be provided.
Sustainable agriculture is defined here as a way of farming that not only protects soil fertility (productivity) and quality of produce, but also other soil functions. In this respect, the ecological soil functions are very important. The soil serves as a habitat for numerous organisms. An important role of these organisms is that together they cause organic matter to be decomposed. Hence, they play an essential role in element cycling processes that should not be disturbed by contaminants. Contamination may be regarded as a stress imposed on the ecosystem. The effect of such stress depends on the type of contaminant, the degree of stress imposed (intensity and duration) and the response of (the most sensitive) organisms. The impact of heavy metals on ecosystems cannot be specified in detail because each ecosystem type may react differently and the effects of individual contaminants may result in different responses (Martin & Coughtrey, 1981). The ecological soil functions overlap with agronomical functions as is the case with *e.g.*, the decomposition of organic residues like crop residues and manure. The resulting release of nutrients and the production of humus contribute to soil productivity.
Another important soil function is the buffer (or filter) function. Soil has a certain (but limited) capacity to bind substances, thus preventing them from leaching. In order to be acceptable, agricultural practices should not result in adverse emissions to other environmental compartments like ground- and surface water. Sustainable use requires that forthcoming generations can also utilize the soil's buffering capacity which should therefore not be 'filled up'.
Heavy-metal inputs need not always be as small as possible since some metals are indispensable for life. According to Alloway (1990), there are three criteria for determining whether or not an element is essential *i.e.*, the organism can neither grow nor complete its life cycle without an adequate supply of the element, the element cannot be wholly replaced by any other element, and the element has a direct influence on the organism and is involved in its metabolism. Copper and Zn are essential elements which may give rise to deficiency problems in plants and animals.
Food plants which tolerate relatively high concentrations of potentially hazardous metals create a greater health risk than those which are more sensitive. In general, it can be stated that food plants are more sensitive to Cu and Zn than to Pb and Cd. Excessive uptake of both essential (Cu, Zn) and non-essential (Pb, Cd) metals may result in adverse effects on soil biota, plants and, due to transfer via the food chain, on mammals, birds and humans.
Since accumulation of heavy metals in soil causes problems when certain soil contents are exceeded, control of heavy-metal fluxes is a prerequisite for sustainable agricultural production. A soil protection policy with regard to heavy metals can be

based on different principles. The state of the soil can be judged by studying relevant soil processes and adverse effects on important soil functions and soil organisms *e.g.*, by a 'pathway analysis' (*e.g.*, Chaney & Ryan, 1993). Such an approach calls for a thorough analysis of soil processes to reveal differences in vulnerability. Another perspective on soil protection is based on a more generic approach by using heavy-metal balance sheets as sustainability indicators (*e.g.*, De Haan & Van der Zee, 1993). This 'balance approach' or 'flux approach' has proven to be very useful in soil fertility studies to discover the depletion of essential elements from soils (Frissel, 1978; Smaling, 1993). In the same way, the balance approach can be used in soil pollution research to discover the accumulation of both essential and non-essential elements in agricultural soils.

The balance approach generally avoids a very detailed study of physico-chemical processes and focusses on 'accumulation' as the primary effect of heavy-metal input and output flows. The use of heavy-metal balance sheets enables a source oriented way of guarding soil quality. Instead of the (desired) status of the soil, the central focal point for analysis is the burdening of the soil with potential toxic elements and the subsequent net accumulation in the soil system.

In this chapter, general aspects of heavy-metal balance studies are described for the agricultural sector. The different quantitative metal balance models distinguish different spatial scales, *i.e.*, (supra) national-, farm-, and field-scale.

Agro-ecosystems

An ecosystem may be defined as a unity in time and space of a community of plants and animals interacting with each other and their abiotic environment (Vereijken, 1992). An ecosystem has a richly detailed budget of inputs and outputs of energy and matter. Because of the lack of precise information about these relationships and the internal functions that maintain the ecosystem, it is often difficult to assess the impact of human activities on the biosphere. A vast number of variables including biologic structure and diversity, geologic heterogeneity, climate and season control the flux of both water and chemicals through ecosystems. Clearly, both living and non-living components of ecosystems are important in defining and regulating the flow of matter and energy within and between ecosystems (Likens & Bormann, 1995).

The farm is a complex system and in many ways similar to a natural ecosystem. Therefore, the term agro-ecosystem implies that subsystems (*e.g.*, insects, birds, micro-organisms) are linked into a food web with the crops and animals of the farm. An agro-ecosystem may thus be viewed as an ecosystem that is used for agricultural purposes. As a relatively simple unit, the agro-ecosystem may be represented by the single farm (Frissel, 1978). However, there is not one single definition of an agro-ecosystem since functional definitions depend on the research or management objectives. Crossley *et al.* (1984) designate individual fields as agro-ecosystems and thus envision the farm as consisting of an assembly of agro-ecosystems. A different view is expressed by Lowrance *et al.* (1986) who envision an agro-ecosystem as a hierarchy of levels (*e.g.*, fields, farms, watersheds and regions) and so a farm is only one level of an agro-ecosystem. The critical constraints for sustainability may depend on these spatial scales as well. If agriculture is analyzed as an hierarchical system, the field scale, farm scale, watershed and landscape scale, and the regional and national scale mainly suffer from agronomic, micro-economic, ecological, and macro-economic constraints, respectively (Lowrance *et al.*, 1986).

Edwards *et al.* (1993) defined a dynamic conceptual model for a farm as a mass flow model with two parallel flow paths through the farm. One pathway is the socio-economic flow with inputs (*e.g.*, land, labor, capital, culture, knowledge) and outputs (*e.g.*, income, health, knowledge, social stability). The other pathway consists of the biophysical flows with inputs (*e.g.*, energy, chemicals, manure, seed) and biophysical outputs (*e.g.*, food, fiber, feed). Also for the internal cycles a distinction can be made between internal socio-economic processes and internal biophysical processes. The biophysical flows and the socio-economic flows are coupled. The cycling of substances (*e.g.*, nutrients and heavy metals) within this complex system is part of the farm management (Edwards *et al.*, 1993). The main purpose of this management is producing a surplus in order to satisfy the demands for food, feed and fibre (Pettersson, 1993), which causes agro-ecosystems to have other qualifications and characteristics than natural ones.

Agro-ecosystems may be viewed as 'domesticated ecosystems' that are intermediate between natural ecosystems (*e.g.*, forest) and fabricated ecosystems (*e.g.*, city). Both agro-ecosystems and natural ecosystems are solar-powered and are composed of the 'components' producers, consumers, and decomposers. Agro-ecosystems differ from natural systems in that they use ever more fossil fuel rather than natural energies (water, wind and horse-power), that diversity (species richness) is greatly reduced by human management in order to optimize yields, that the dominant plants and animals are under artificial rather than natural selection, and that control is governed by the aims of man (*i.e.*, external) rather than internal via subsystem feedback and self-regulation as in natural ecosystems. Agro-ecosystems resemble urban-industrial systems in their extensive dependence and impact on externals since they have both large input (*e.g.*, fertilizers and pesticides) and output (biomass production, emissions) environments (Odum, 1984). Because agro-ecosystems are very complex organisations of organisms and are characterized by many interactions, metal transfers in agro-ecosystems are highly complex as well (Ross, 1994). Due to the dependency on natural conditions and processes, the role of human management in farming processes will always be less efficient than in industrial processes that are not subject to these environmental influences (Pettersson, 1993).

Substance flow analysis

Substance policy is especially relevant for persistent substances that, after emission to the environment, may accumulate or further dissipate in the environment. Substance flow analysis (SFA) is an instrument for substance policy that is based on the law of conservation of mass and consists of an integrated examination of all flows of a substance or a group of substances within a defined geographic system, encompassing both its economy and its environment (Kleijn *et al.*, 1994). The goal of SFA is to support data acquisition (check on errors and identification of missing flows), to analyze trends and their causes (major flows and origin analysis) by monitoring, and to support pollution abatement measures.

Analyses which couple substance flows through economy and environment may be carried out in several ways. One way is to start with the environmental problems that are related with a certain substance and then to trace back the origins (sources and causes) in the economy. Another way is to start with economic activities and to investigate the environmental consequences of these activities. In this way, current and future substance and material flows through the economy serve for scenarios about future environmental burdens. Substance flow analysis is more comprehensive than the conventional balance approaches since it relates actual problem flows in the environment to economic processes and, by determining the accumulation in the economy, potential future problems are recognized early. Thus, SFA extends the concept of biogeochemical cycles to 'anthropo-biogeochemical' cycles (Van der Voet, 1996). However, SFA does not provide information about costs and other economic or societal aspects and hence a coupling with economic models may be difficult to realize.

Problem shifting is the displacement of a problem to another environmental compartment, another area or another time (context). The solution to a problem often amounts to no more than a shifting of the problem and thus the perceived solution is only apparent. One of the strengths of SFA is the possibility to trace down the shifting of environmental problems within one substance flow. However, since only one substance or group of substances is described, it is hard to investigate the results of substitution (Van Gerwen *et al.*, 1995). Thus, problem shifting to other substance chains cannot be investigated with this tool (Van der Voet, 1996).

Substance flow analysis is placed in the field of industrial ecology (IE) and industrial metabolism (IM). Industrial metabolism draws an analogy between the economy's metabolism to create 'technomass' and the biosphere to create biomass. It traces the movement of chemicals through the industrial economy (including agriculture), identifies the entry points through which they pass from the economy to the environment, and assesses their impact once they have entered the environment. Both the biosphere and the industrial economy are systems for the transformation of materials. One of the insights gained in IM studies is that a large number of material uses (*e.g.*, fertilizers, pesticides, heavy metals) are inherently dissipative (Ayres, 1989). River basin studies have shown that the origins of water pollution have been shifting from industrial (point) pollution to consumer (diffuse) emissions over the past few decades (Stigliani, & Anderberg, 1992). Because IM analyses are based on the principle of conservation of mass, problem-shifting is readily exposed (Stigliani & Jaffe, 1993).

The IE concept was first introduced by Frosch & Gallopoulos (1989) as an analogy between natural ecosystems and industrial systems. Industrial ecology aims at an optimization of energy and materials use and at waste minimization in industrial and consumer activities. Graedel & Allenby (1995) posed that examining the totality of relations between economic activity (industrial metabolism) and the environment (environmental metabolism) requires that an economic activity *(e.g.*, mining, manufacturing, agriculture) is not viewed in isolation from its surroundings but that the interactions are studied also.

The Dutch Council for Environmental Management (CFEM) distinguishes three different levels of IE. Based on the perspectives of Graedel and Allenby (1995), the CFEM (1996) defined the conceptual view on IE as a perspective on society, in which industrial, agricultural and consumer activities can be organized according to the same principles as natural ecosystems (*e.g.*, exchange via strategic cooperation) in such a way that energy and materials can be used, exchanged and recycled more efficiently. Industrial ecology may also be viewed as an analytical methodology. It then studies substance, material and energy flows at basic and aggregated levels as a further development of the concept of IM. Industrial ecology as a management strategy, focusses on saving of materials and energy through 'inter-product-chain-exchanges' (CFEM, 1996a).

The complexity of the substance flows renders a complete analysis impossible. A rather elaborated study on heavy-metal flows and accumulations in economy and environment in the Netherlands has been undertaken by Guinée *et al.* (1998). In this thesis, we restrict 'economy' to agro-ecosystems, which form only a part of the agro-economic substance chain. Consequently, the environmental flows are studied to a limited extent as well.

Substance flow analysis of agro-ecosystems

Substance flows in ecological systems have been studied for a long time (*e.g.*, the global biogeochemical cycles of carbon (C), nitrogen (N), phosphorous (P), and sulfur (S)). The tradition within statistics of detailed bookkeeping of flows and stocks of agricultural products resulted in mineral balances for the Netherlands derived by the National Bureau of Statistics (CBS: Olsthoorn, 1992). These were later followed by the studies of Cu (CBS, 1987), Zn (Gorter, 1991), and Cd (CBS, 1994) in the agricultural sector.

Agro-ecosystems receive heavy-metal inputs from various sources that differ in importance for different metals, different systems and different soils. Input flows are caused by primary (*i.e.*, economic) and secondary (*i.e.*, inputs via the environment) sources. Primary sources are part of the material flows that come from industry (*e.g.*, mineral fertilizers, feed), trade (*e.g.*, straw, animals, manure), waste management (compost), and waste water management (sewage sludge). Within the group of primary sources a distinction can be made between intentional inputs (*e.g.*, Cu-compounds used as pesticide or fertilizer) and unintentional inputs (*e.g.*, Cu as a constituent of soil amendments, like manures). Since primary sources consist of means of production, *i.e.*, purchased and self-processed materials, they may be controlled to some extent. Secondary sources always cause an unintentional and uncontrollable input into agro-ecosystems, like in the case of atmospheric dry and wet deposition of heavy metals and sedimentation after inundation in areas that are regularly flooded. The distinction between primary and secondary sources can be used for taking reduction measures that are aimed at the right target group.

Output proceeds via marketing produce (trade) and via losses to the external environment. The output via produce depends on the farming system. For example, the output from dairy farms is notably smaller than from arable farms (Van Driel & Smilde, 1990). The outputs will reach the consumers through the trade and retailing chain. Losses to the external environment are mainly due to processes like leaching, wind erosion and surface runoff.

Heavy-metal balance sheets show the budget of all heavy-metal in- and outputs, which make them a useful tool to make an integrated evaluation of all heavy-metal inputs by different sources and an analysis of the partitioning of the metal influx between accumulation in the topsoil, leaching to the subsoil and crop uptake. Proper use of heavy-metal balances requires attention being paid to the definition of the system, the reliability of data from literature and measurements, quantification, data presentation, and interpretation of the balance in view of sustainability.

Definition of the system

For a proper system identification, it is necessary to know which entities are part of the system, which external entities influence it, how the entities within the system relate to each other, and how the entities within the system relate to the entities outside of the system.

In view of the diversity of the relations with the external surroundings, the agro-ecosystem can be typified as an open system. The boundary of a system is the imaginary line seperating what is considered to be inside the system and what is considered to be outside. The heavy metals pass between the compartments (*e.g.*, plant, animal, soil) along certain pathways and the quantification of these transfers requires a definition of the system boundaries in time and space. The behavior of elements in agro-ecosystems may thus be evaluated from rates of transfer across the system boundaries and between the main compartments.

The single farm has, in principle, easily recognizable boundaries. The agricultural activities at the single farm (or field) level consist of animal production and/or crop production. The system is open to the atmosphere and the upper side of the farming systems is formed by crops and buildings. Its lateral borders are defined by the farm gate (property boundaries) or by surface waters.

The appropriate system boundaries of heavy-metal flows and cycles may be defined for different spatial and temporal scales. With regard to the temporal boundary, it is impossible to choose a time-base to suit the rates of all processes. Thus, the chosen timebase will always be somewhat arbitrary like *e.g.*, one year (*i.e.*, growing season) or one crop rotation. The interactions between current, preceding and subsequent crops justifies the drawing of system boundaries around a crop rotation rather than around a particular crop. With regard to the spatial (physical or topographical) boundary, it may be that the same entities are both part of the economic system and part of the natural environment since the different functions of the system can hardly be separated with respect to the economic and the ecological subsystems. For example, the topsoil is defined as the upper part of the soil (ca. 0.3 m) that is intensively used by man (*i.e.*, the plough layer). The plough layer can be included within the system boundary since it is an integral part of the agricultural production system (economic function). Moreover, the farming activities change the soil's quality which in turn influences the output. However, the plough layer may also be viewed as being part of the external (or natural) environment that serves as a habitat for many organisms (ecological function). In that case, it is separated from the agro-ecosystem and all flows into the plough layer should then be considered as output flows to the environment.

If the plough layer belongs to the agro-ecosystem, heavy-metal input to and accumulation in the topsoil should not be defined as an emission to the external environment. However, soil presently in agricultural use may be set aside or converted to other uses. In such a case of changing land use the accumulated heavy metals become part of 'the environment' and turn out as an emission all of a sudden. Agricultural uses thus may result in heavy-metal contamination of the environment directly through losses from the plough layer or indirectly by land use changes. This shows that distinctions between agricultural soils and others are artificial in some respects.

The reliability of data from literature and measurements

Heavy-metal balance studies tend to suffer from a lack of good quality (recent and accurate) data and hence unreliable, averaged or estimated numbers are being used, which renders the calculation of reliable heavy-metal balances impossible.

Table 2.1. Heavy-metal contents of agricultural amendments (mg kg^{-1} dry weight).

	Cd	Cu	Pb	Zn
Sewage sludge	<1-3410	50-8000	2-7000	91-49000
Composted refuse	0.01-100	13-3580	1.3-2240	82-5894
Animal manure	0.1-0.8	2-172	0.4-27	15-566
P-fertilizer	0.1-190	1-300	4-1000	50-1450
N-fertilizer	0.05-85	-	2-120	1-42
Lime	0.04-0.1	2-125	20-1250	10-450

Source: Ross (1994)

Literature data often show large variations, causing a need for improving quality and quantity of the required data so as to improve on estimates and best guesses. Variations that may occur are shown in Table 2.1.

Quantification
In principle, all relevant (material or substance) flows can be measured or estimated. In practice, there is a problem in giving a 'full picture' because of uncertainties with regard to certain flows. Leaching is one of the most difficult flows to quantify reliably by measurements or models. Therefore, in most balance studies, leaching is either neglected or simulated in a simplified way.
A static balance is comparable to a black box model which serves to find relationships between input and output of a system, without knowing the system's structure and behavior. In a black box model, the input-output relationships are determined by some transformation function. In the case of soil, this transformation function is not constant due to changes in the soil's buffering capacity etc. The influence of system's properties on the output in time is determined by the system's and compound's behavior. The state of a system at a moment in time is the set of relevant properties which that system has at that time. This state needs to be known in order to predict, with a given input, the output (deterministic) or the probability of a certain output (stochastic) in the course of time. This is attempted in dynamic modeling (further details on static and dynamic balances are provided in Chapter 4).

Data presentation
A standard format for data presentation enables a comparison between systems and hence a broader interpretation of the results. Agricultural systems may be characterized according to their type (dairy farming, arable farming, mixed farming, etc.), their philosophy (conventional, integrated, ecological) and their 'intensity' (input-output characteristics: intensive, extensive, self sustaining). The difference between 'intensive' and 'extensive' may be based on the use of (raw) materials (*e.g.*, fertilizers and pesticides), the use of energy, the use of nutrients, and the output. Frissel (1978) describes several agricultural systems that differ with regard to all these characteristics. These system characteristics may be compared with the resulting heavy-metal accumulation in soil, leaching, offtake by plants, uptake by animals, etc. Based thereon, a classification of farming types and corresponding heavy-metal flows may be made. Such a classification should also take into account soil characteristics since different agro-ecosystems have a different soil use and may also be located on different soil types.
The framework of a SFA can be visualized in a substance flow diagram (SFD), which is divided into environmental and economic subsystems. This diagram (Fig. 2.1) may be used for making an inventory of economy/environment interactions and of transfers of substances from a source to a sink (Udo de Haes *et al.*, 1988). A distinction is made between stocks of substances (bold rectangles), flows of substances (arrows), environmental media (parallellogram), and processes involved

in changing and subdividing substance flows (rectangles). The double arrow at the mobile (economic and environmental) stocks signifies accumulation and desaccumulation. The double arrow at the immobile (economic and environmental) stocks resembles processes of mobilization and immobilization.

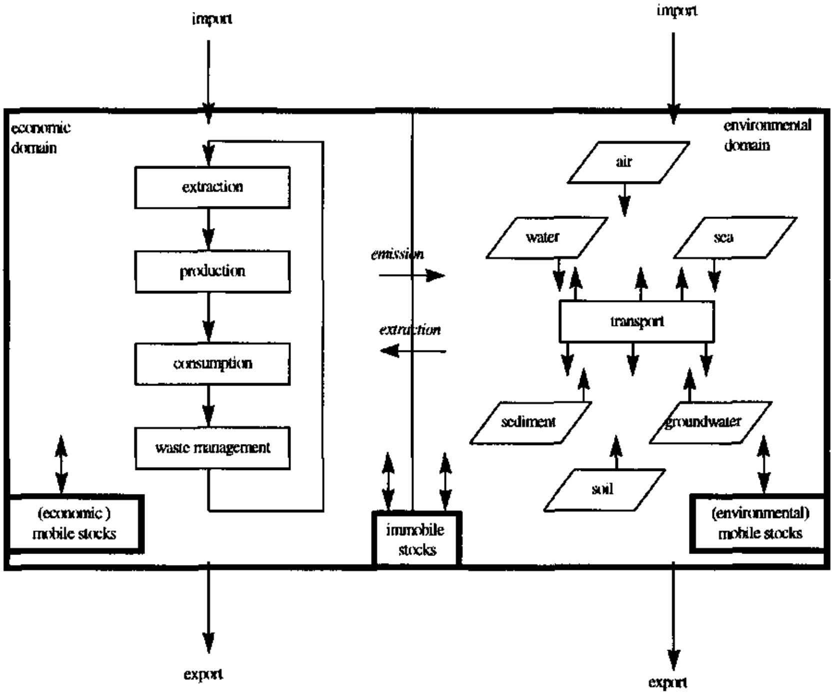


Figure 2.1. The Substance Flow Diagram (adapted from Guinée *et al.*, 1998).

This general SFD may be specified for different agro-ecosystems (Chapter 6).

Interpretation of the balance in view of sustainability
The difference between input flows (I) and output flows (O) determines the resulting accumulation (expressed as I-O or I/O). Although accumulation indicates that the system is off balance, accumulation per se as a primary effect only reveals that there is an absolute increase in the soil's stock (S). Relating accumulation to the total amount of metals in the soil ([I-O]/S) already gives some more insight in the potential risk for environmental problems in the future since it shows the relative (or percentual) stock increase (*i.e.*, ΔS). In order to calculate the resulting change in soil content (ΔG) from the stock increase, it is necessary to know the soil bulk density and the thickness of the mixed layer as well. These (location specific) soil parame-

ters may not be constant in time.

An analysis of heavy-metal flows and resulting (absolute or relative) accumulation should be followed by an analysis of what happens in the soil in order to predict the effects of accumulation on human and ecosystem health (*i.e.*, 'environmental quality'). Hence, indicators that relate effects on different environmental compartments require consideration of the relevant physico-chemical processes in a long-term perspective.

If an element is naturally abundant (*e.g.*, iron and aluminum) and accumulates in a chemical form of similar solubility to its natural compounds, accumulation may proceed without any appreciable effect on the system itself, its produce or on the environment. However, accumulation of Cd, Cu, Pb, and Zn mostly involves a steady increase in activity and/or mobility in the soil. The rate of this increase depends on the soil's buffering capacity and on the actual surplus on the balance sheet. Accumulation of these elements thus leads to an increase in element flows between the system compartments (resulting in increasing contents in produce) and from the system to its surrounding environment (Van Riemsdijk *et al.*, 1987). Since cycling features may be modified, both mass balances and transfer rates should be considered. The dynamics of elements' pathways and transfers between the different pools are determined by their solubility in water, their degree of chemical reactivity, conditions within the system and by the physical and chemical environment. This results in different cycling characteristics for different elements (Frissel, 1978) and thus a system may be in different states of balance for different elements at the same time (Van Riemsdijk *et al.*, 1987).

Since balance studies try to avoid to account for the above mentioned processes in a detailed manner, another way to account for 'risks' or effects is to make use of existing standards that are related to the toxicity of the metals. If the critical soil content is expressed as G_{crit}, the rate of reaching this critical value equals $\Delta G/[G_{crit}-G]$. This kind of calculations may be carried out *e.g.*, by using standards of the European Community (C.E.C., 1986) and the United States EPA (USEPA, 1993).

Apart from the problem that these standards do not always have a sound scientific basis (as is discussed in McGrath *et al.*, 1994), another setback of this approach is that the resulting rates are usually based on static balance calculations (using constant output rates), whereas in reality the output flows (*e.g.*, by leaching and crop offtake) are dynamically related to the soil content in the case of Cd, Cu, Pb and Zn. Therefore, Moolenaar *et al.* (1997a) derived indicators of sustainable heavy-metal management in agro-ecosystems from a dynamic soil balance. These indicators provide insight in the relative importance of different heavy-metal flows and allow priority assessment of protection measurements and quantification of the gains of management options that aim at preventing quality standards for soil, crop, and groundwater from being transgressed. An interesting finding was that even if the total input currently does not exceed the total acceptable output, problems may still occur in the long run (further details are provided in Chapter 9).

Another aspect with regard to the interpretation of heavy-metal balances is also very important for SFA studies. The substances which are studied (*i.e.*, heavy metals in this case) are mostly part of materials which serve as their carriers. In order to study certain substances it is thus necessary to carry out a material flow analysis (MFA) at the same time. The carriers or materials which are studied in MFA may be very important for the resulting SFA. For example, Cd may be 'carried' by P-fertilizers and by refuse compost. Due to the great differences in the matrices of these materials, these different types of carriers influence the form and rate of Cd accumulation in soil (Moolenaar *et al.*, 1997b; Chapter 5).

Conclusion

It is important to carry out substance flow analyses of agro-ecosystems in order to get a comprehensive view of actual and potential future problem flows in their economy and environment. A consistent approach is needed in order to calculate heavy-metal balance sheets and to reveal the consequences of heavy-metal flows within the defined system by quantification of flows, data presentation and interpretation of the balance in view of sustainability.
In Chapter 3, heavy-metal balance studies on different spatial scales in several European countries are presented in order to discover the possibilities for an effective heavy-metal management.

CHAPTER 3

BALANCING HEAVY METALS. II. HEAVY-METAL BALANCES AND -MANAGEMENT IN EUROPEAN AGRO-ECOSYSTEMS

Abstract

In order to determine the options for a sustainable heavy-metal management in agriculture, heavy-metal balance sheets are used as a means to quantify the heavy-metal flows in agro-ecosystems. General aspects of heavy-metal balance studies in agro-ecosystems were described in Chapter 2. In this chapter, several European studies on heavy-metal balances on different spatial scales and in different agro-ecosystems are reviewed. Implications for an effective heavy-metal management of agro-ecosystems are disussed.

Heavy-metal flows on different spatial scales

Heavy-metal flows in agro-ecosystems can be analyzed on the field scale, the farm scale, the regional or the (supra-) national scale. These different scales may show different 'problem flows'. For example, Cd can enter the system by P-fertilizers, deposition and sewage sludge. In a study for the Dutch province of South-Holland (Van der Naald *et al.*, 1989), these flows proved to be most important on the national, the regional and the local scale, respectively. Thus, the scale on which processes are studied may influence the outcomes significantly and differentiation is necessary for taking appropriate measures at the right place.

Analysis on the (supra-) national scale

The national balance is calculated by subtracting all the heavy-metal flows leaving agriculture from all the heavy-metal flows entering agriculture. Thus, the total net input of heavy metals to the (agricultural) soil is calculated for agriculture as a whole and one gets an overview of this 'average burden' on the 'average agricultural soil' by applying national statistics on feedstuffs, mineral fertilizers, animal manure, agricultural products (milk, meat, crops), etc. Using annual sales, mean concentrations (*e.g.*, in crops or fertilizers), mean application rates, and mean yields per crop, the mean annual loads in a certain region can be calculated.
This method allows for tracing down the most important heavy-metal flows and bottlenecks on a regional to (supra-) national scale. Clearly, analyses at the national level do not give due attention to relevant processes on a smaller scale, because the local and site specific aspects with regard to soil characteristics (*e.g.*, adsorption capacity, hydrological properties) and soil use (*e.g.*, inputs and crop rotation) are averaged out.

Analysis on the farm scale

The farm-gate balance shows the characteristic flows and processes of the farm as a whole. Since large differences exist for different metals between and within farming systems, the farm-gate balance offers a way to finetuning heavy-metal management directly at the farm level.

Analysis on the field scale

The field-scale balance shows the heavy-metal balance for the soil compartment or the plough layer of individual fields. An analysis on the farm scale does not distinguish the soil, animal and plant compartments within the farm boundaries. These compartments have different input and output flows, which differ largely between farming systems. Inputs of the animal compartment consists of feed and litter (used indoors), consumption of harvested crop (roughage), and grazing of forage. Eggs, milk meat and manure are the outputs. The inputs of plants are related to uptake and atmospheric deposition, while the output of this compartment is the consumption by grazing or harvesting of the plants themselves as primary products.

The flows between the farm compartments (*i.e.*, internal flows) are not accounted for in a farm-gate balance. If these internal flows play an important role, as is the case in dairy and mixed farming, the farm-gate balance differs from the field-scale balance.
A balance of heavy metals on the field scale relates the rates of accumulation, inputs and outputs. The input and output rates are a function of soil and management characteristics, which can be derived for individual fields.

Heavy-metal balance studies in several European countries

The Netherlands
In the Netherlands, somewhat more than half of the land area (*i.e.*, ca. 2 million hectares) is being used for agriculture. The main soil types in the Netherlands are sand (ca. 42%), clay (ca. 40%) and peat (ca. 13%) soil.
Van Driel & Smilde (1990) calculated the heavy-metal balance sheets for different scenarios in Dutch agriculture and found that the total heavy-metal supply by far exceeded the losses for most fertilizer plans and cropping systems. Regarding arable farming, they concluded that substituting animal manure for mineral fertilizer increases heavy-metal supply (except for Cd), that heavy-metal supply and losses balance (except for Cd) if mineral fertilizers are used only and that total heavy-metal supply (including deposition) exceeds losses. Moreover, their comparison of Dutch Cd balance studies in different years concerning arable farming revealed large differences in the estimated values for crop offtake and for leaching.
Regarding dairy farming, the number of cows per hectare and the use of feed concentrates or roughage (silage maize) determine the balance. They concluded that using pig and poultry manure strongly increases heavy-metal supply, that supply via concentrated feedstuffs alone approximates or exceeds total losses and that supply of heavy metals with mineral fertilizers is relatively small.
A large-scale assessment using existing national bookkeeping systems was carried out by Poppe *et al.* (1994). Using the results of the national monitoring system on mineral balances they first calculated the (average) heavy-metal flows per farm and farming system. The bookkeeping methodology views the load of agricultural soils as the net difference between heavy-metal input and output at the farm-gate. The differences between the systems are large and in all systems the heavy-metal inputs exceed the heavy-metal outputs (Table 3.1). Then, they aggregated their farm-scale results to the national level by multiplying the number of farms of a certain farming system with their respective heavy-metal flows. This resulted in quite different numbers as compared with the national balance of the National Bureau of Statistics (CBS). One of the reasons is that the bookkeeping data do not represent all farms and therefore the aggregation results should be viewed with care.

Table 3.1. Input (I), output (O) and net input (N) of heavy metals (kg yr^{-1}) averaged per farm and farming system in 1990/1991.

	Arable	Grass	Mixed		Arable	Grass	Mixed
Cd:				Cu:			
I	3.48	2.3	1.89	I	11.9	7.0	12.6
O	0.06	0.03	0.14	O	1.9	0.5	4.0
N	3.42	2.26	1.76	N	10.0	6.5	8.6
Pb:				Zn:			
I	0.31	0.14	0.14	I	35.7	21.4	30.6
O	0.05	0	0.02	O	10.2	1.9	11.2
N	0.26	0.14	0.11	N	25.5	19.5	19.4

Source: Poppe *et al.* (1994)

Van Erp & Meeuwissen (1994) studied the effect of fertilizer plans on heavy-metal additions. A fertilizer plan is defined as a combination of mineral and organic fertilizers aiming for an optimal crop yield and maintaining soil fertility. Farming systems, crop rotation, soil type and fertilizer use were representative for the Dutch situation. They found that heavy-metal input strongly depends on the farming system and that the input increases in the order of dairy farming < continuous maize ≈ arable farming. Also, there were big differences between fertilizer plans (factor 2-5 on average) even within farming systems. This results from varying heavy-metal contents in mineral fertilizer (production process and contents in raw materials), manure (composition of feedstuff), compost (raw materials, different production processes), and feedstuffs (different ways of analysis).

The CBS found that the total Cu input was about four times higher than the Cu output in the period 1981-1985 on a national scale (CBS, 1987). A significant percentage of the Cd, Cu and Zn inputs results from animal manure applications. Cu and Zn are added (suppletion) to feed concentrates in great quantities (CBS, 1987; Gorter, 1991). Cd is added with feed phosphate. From 1980-1990, input reduction of heavy metals was aimed at by decreasing Cu and Zn contents in feed, decreasing Cd contents in mineral fertilizers and feed phosphate, and by decreasing Pb in benzine. The national balance of heavy metals was calculated by Van Eerdt and Stiggelbout (1992) for 1980 and 1990 (Table 3.2).

Table 3.2. Total heavy-metals input to agricultural soil (ton yr^{-1}) in the Netherlands.

	Cd		Cu		Pb		Zn	
	1980	1990	1980	1990	1980	1990	1980	1990
Manure	6	4	1050	750	70	60	1800	1800
Mineral fert.	7	2.5	150	120	10	10	150	140
Deposition	5	3	80	50	260	120	500	310
Sewage sludge	1	0	39	35	27	15	115	110
Pesticides	0	0	35	11	0	0	60	68
Hunting/sports	-	-	-	-	220	230	-	-
Total	19	9.5	1360	970	600	450	2640	2440

Source: Van Eerdt & Stiggelbout (1992)

De Boo (1995) calculated national heavy-metal balance sheets for Dutch agriculture in 1992. The main fertilizers were animal manure (85 million ton FW) and mineral fertilizer. Sewage sludge and composts only constituted ca. 3.5% (3 million ton FW) of the total of organic fertilizers. More than 95% of the total heavy-metal inputs was due to mineral fertilizer and (imported) feedstuff (Table 3.3).

Table 3.3. Heavy-metal balance sheets for Dutch agriculture in 1992 in ton yr^{-1}.

	Cd	Cu	Pb	Zn
Mineral fertilizers	2.87	112.5	16.5	115.9
Feedstuff (import)	1.17	655.0	16.3	1755.4
Organic fertilizers	0.15	11.0	4.0	100.0
Total input	4.19	778.5	36.8	1971.3
Feedstuff (export)	0.12	83.1	1.5	186.5
Produce (crop)	0.77	5	1.7	17.6
Produce (animal)	0.03	9.1	0.13	169.7
Total output	0.92	97.1	3.3	373.7
Accumulation				
ton yr^{-1}:	3.3	681.4	33.5	1597.6
g ha^{-1} yr^{-1}:	1.6	340	17	800

Source: De Boo (1995)

For all four metals this study showed that the ratio of input over output varied between a factor 1 to 10. Relatively, the input with organic fertilizers (excluding manure but including compost and sewage sludge) was of minor importance. Feed concentrates are imported and then used for feedstuff production. Imported feedstuffs are mainly used for pigs and poultry, but the pig and poultry manure is applied to arable and grassland within the Netherlands. 64% of the Cd input resulted from mineral fertilizers. 79% and 86% of Cu and Zn inputs respectively resulted from imported feedstuff.

In a recent survey (IKC, 1997), the most important organic and mineral fertilizers were analyzed in order to obtain more recent and reliable data. Based on these measurements, the inputs to agricultural soils in 1994/1995 by feed concentrates and mineral fertilizers were estimated to be for Cd 1.4 and 2.0, for Cu 760 and 70, and for Zn 1683 and 60 (ton yr^{-1}), respectively. Although the Cd contents in feed concentrates are lower than in mineral P fertilizers, the large amount of manure applied results in Cd inputs that are about the same order of magnitude as inputs with mineral fertilizer.

To reduce an undesirable heavy-metal accumulation in arable soils, the proposed Dutch governmental policy is to aim at an input of heavy metals via mineral and organic fertilizers that does not exceed the output of heavy metals via removal of harvest products and by-products (Anonymous, 1991a). The choice of fertilizer materials in a fertilizer plan is of great importance for the input of heavy metals. Optimization models can be used to develop fertilizer plans which meet constraints on heavy-metal input via fertilizers, but also on other agricultural, legislative and economic constraints. Because of the complexity in decision making, a decision support system is needed that provides knowledge on the effects of agronomic, environmental, legislative, economical and farm-specific factors on fertilization in arable farming systems.

Velthof *et al.* (1996) used such an optimization model and their calculations indicate that it is not possible to achieve fertilizer plans in which the Cd, Cu and Zn input and output balance for all three metals at the same time. Minimizing the Cd input will increase Cu and Zn inputs and minimizing Cu and Zn inputs will increase the Cd input due to substitution processes of animal manure and mineral fertilizer.

The cited studies show that mostly leaching and deposition are not taken into account in heavy-metal balance studies. One reason is that these flows are not considered as being part of the 'agricultural balance'. Another reason is that both atmospheric deposition and leaching are difficult to quantify. Due to the large variation in deposition numbers and even more uncertainty regarding leaching it is hard to tell whether leaching and deposition balance or not. Some large differences that exist with regard to measured/calculated values for atmospheric deposition are shown in Table 3.4.

Table 3.4. Mean atmospheric deposition in the Netherlands in 1990 (g ha^{-1} yr^{-1}) according to different studies based on measurements (1) or calculations (2 and 3).

	1	2	3
Cd	1.5	0.9	1.3 (0.9-1.9)
Cu	25	4	8.9 (5.7-14)
Pb	60	38	144 (100-190)
Zn	155	121	72 (49-110)

Source: Lijzen & Ekelenkamp (1995)

Denmark

The Danish EPA (DEPA, 1994) calculated national balances for Cd and Pb in 1990 (Table 3.5).

Table 3.5. Cd and Pb flows to the Danish soil in ton yr^{-1}.

	Cd	Pb
Deposition	4.7	240
P-fertilizer	2.6	-
Agricultural chalk	1	-
Sewage sludge	0.1	6
Ammunition	-	600-700
Scrap storage and other sources	-	700-4000

Source: DEPA (1994)

Hovmand (1984) calculated Cd, Cu, Pb, and Zn balances for Danish agriculture. Tjell & Christensen (1992) updated his work to 1990 with regard to Cd. The main part of Danish crops are used as animal feed (fodder) and are returned as manure. A minor part of the harvest goes to human consumption (Hovmand, 1984). Therefore, leaching is the only significant outflow. The conclusion that phosphate fertilizers and atmospheric deposition are the main inputs (1.5 and 1 g ha^{-1} yr^{-1} respectively) remained the same. The absolute accumulation decreased from ca. 10 g ha^{-1} yr^{-1} in the early 1970's to ca. 4 g ha^{-1} yr^{-1} in 1980 and ca. 1.5 g ha^{-1} yr^{-1} in 1990 due to a dramatic reduction of atmospheric deposition to around 1 g ha^{-1} yr^{-1} in 1990. Also, the fertilizer input was reduced due to a combination of lower consumption of P-fertilizer and a lowering of the average Cd concentration in the P-fertilizers.

Tjell & Christensen (1992) estimated that the range of accumulation varied between less than zero to over 4 g ha^{-1} yr^{-1} with a mean value of ca. 1.5 g ha^{-1} yr^{-1}. The variation in Cd losses by leaching is substantial and varies between 1.5 to 3.5 g ha^{-1} yr^{-1} in the more humid western part of Jutland with relatively acid sandy soils and between 0.3 to 1 g ha^{-1} yr^{-1} in the eastern part of Denmark with moderate rainfall and neutral soils.

Sweden

Andersson (1992) estimated heavy-metal fluxes in agricultural soils (2.6 million ha) in order to calculate heavy-metal balances for Sweden in 1990. The main crops (total area) in Sweden are ley (39%), barley/oats (29%) and wheat/rye (13%). With respect to agricultural practices, there is a distinct north/south gradient over the country. In the southern part of Sweden, mainly cash crops are grown. On the less fertile soils in the (southern and) northern parts, mainly livestock farms (cattle) have been established. Mixed farms (mostly small) are found in both the northern and southern part of the country.

The fundamental dividing line between farming based on livestock and farming based on cash crops also results in different heavy-metal balances. In the areas where cash crops are grown, there is a slow depletion of Cu and Zn since mainly commercial fertilizers are used instead of animal manure. In the northern part, straw is harvested and used as a feed or litter for livestock. The consequent utilization of manure and the subsequent crop removal are important for the internal (*i.e.*, on farm) Cu and Zn circulation. However, a net contribution originates from Cu and Zn in mineral feeds and external fodder additives.

With regard to manure, Andersson (1992) found that 'the uncertainty as to the rates of application as well as the contents is embarassing since manure is the dominating source of several elements.' He found that the (combined) removal in crops and by leaching differ for different crop rotations and for different agricultural districts (Cd: 0.27-0.73; Cu: 27-48; Pb: 1-7; Zn: 147-228 g ha^{-1} yr^{-1}). The annual alteration in heavy-metal contents of agricultural soils in 1989/1990 for different regions and crop rotations (g ha^{-1}) is shown in Table 3.6.

Table 3.6. Input (I), output (O) and net input (N) of heavy metals (g ha^{-1} yr^{-1}) averaged per farm and farming system, 1989/90.

Farming system:	A	B	C	D	E
Cd					
I	1.97	1.52	1.97	2.09	1.46
O	0.7	0.27	0.73	0.55	0.41
N	1.27	1.25	1.24	1.54	1.05
Cu					
I	14.7	9.9	91	94.9	91
O	40.3	27.3	47	48.3	35.3
N	-25.6	-17.4	44	46.6	55.7
Zn					
I	128	101	527	542	504
O	221	162	228	209	147
N	-93	-61	299	333	357
Pb					
I	35.8	22.7	28.6	36.6	21.6
O	2.4	0.87	6.0	7.0	5.2
N	33.4	21.8	22.6	29.6	16.4

Source: Andersson (1992);
A: plain district S. Gotaland (arable: 13 kg P ha^{-1} yr^{-1});
B: Southeast Gotaland; plain district. N. Gotaland; plain district Svealand (arable: 11 kg P ha^{-1} yr^{-1});
C: Southeast Gotaland; plain district N. Gotaland; plain district Svealand (mixed: 8 kg P ha^{-1} yr^{-1});
D: forest district Gotaland (livestock: 8 kg P ha^{-1} yr^{-1});
E: N. Sweden (livestock: 6 kg P ha^{-1} yr^{-1}).

Finland

Finnish soils have some distinguishing features with respect to chemical characteristics. The average pH-H_2O is low and equals 5.8. The average organic matter content is high and equals 9% (FMAF, 1997).

Mäkela-Kurtto (1996) derived heavy-metal balances for Finnish agricultural soils (1.8 million ha) based on data on sales numbers, application rates, average contents, amounts manure generated, and crop yields (Table 3.7). Water erosion (runoff) is a very important flow on these balances since the averaged loss of soil solids is estimated to be 500 kg ha^{-1} yr^{-1}. Depending on slope, soil type and precipitation, this number may vary between 50 and 7000 kg ha^{-1} yr^{-1}. Lime applications are estimated to be 450 kg ha^{-1} yr^{-1} on average. Heavy-metal contents in manure (2 million ton DW) are taken to be 0.2, 65, 250, and 3.3 mg kg^{-1} for Cd, Cu, Pb, and Zn, respectively. Kemira sold 34162 ton P-fertilizer with a very low Cd content varying between 1 to 5 mg Cd per kg P.

Table 3.7. Heavy-metal balances of Finnish cultivated soils (g ha^{-1} yr^{-1}).

	Cd	Cu	Pb	Zn
Soil content (mg kg^{-1})	0.21	21	16	36
Deposition	0.15	5.9	7.5	15.7
Fertilizers	0.10	100	1.2	91
Manure	0.22	72	3.7	278
Lime	0.03	2.3	1.7	11.6
Sludge	0.02	6	0.6	12.2
Total in	0.52	186.2	14.7	408.5
Crops	0.14	18.7	0.75	115
Leaching	0.06	4.3	0.5	8
Runoff	0.11	10.5	8	18
Total out	0.31	33.5	9.25	141
Accumulation	0.21	152.7	5.5	267.5

Source: Mäkela-Kurtto (1996)

Austria

Reiner *et al.* (1996) calculated heavy-metal balances at field and farm level on 24 farms in upper-Austria which together represented the most important farming types for that region (Table 3.8). The different farms (*i.e.*, arable, cattle, pigs, and mixed cattle/pigs) applied compost, sewage sludge, manure or mineral fertilizer as their N and P source. The calculations were based on materials accounting of these amendments for every individual farm in 1995. The amounts of fertilizers, crop type, yields, etc. were determined by information on buying and selling (invoices) and by literature data on heavy-metal contents of these materials.

Table 3.8. Mean heavy-metal accumulation on examined farms (g ha^{-1} yr^{-1}) due to different fertilizers.

	Cd	Cu	Pb	Zn
Compost	8 (4-9)	600 (200-1000)	440 (230-630)	2800 (1100-3900)
Sludge	6 (3-9)	700 (100-1400)	210 (170-250)	2500 (500-4300)
Manure	5 (4-7)	300 (100-500)	170 (160-185)	1200 (700-1800)
Min. fert.	4.5 (3-6)	40 (30-50)	160 (160-170)	300 (200-300)

Source: Reiner *et al.* (1996)

These results (Table 3.8) show that conclusions with regard to farm type (based on amendments) cannot be drawn since the differences between single farms within a certain farm type were often higher than the differences between these four types. However, these outcomes show that there is a potential for optimizing the agricultural practices at the level of the individual farm. Reduction of use and emissions of heavy metals may begin at the design of processes and products on individual farms (Reiner *et al.*, 1996).

Germany

Wilcke & Döhler (1995) calculated average heavy-metal balances for the (formerly western) German agriculture in 1995 (Table 3.9).

Table 3.9. Heavy-metal balances of German agriculture in 1995 (g ha^{-1} yr^{-1}).

	Cd	Cu	Pb	Zn
Weathering	0.1	3.5	0.8	2.3
Deposition	2.5	52.6	57.2	540
Mineral fertilizer	1.5	9	10	65.6
Irrigation	0.01	0.1	0.1	4.1
Sewage sludge	0.14	13.7	6	55
Compost	0.0	0.03	0.04	0.13
Feed (import)	0.04	0.95	0.73	3.56
Other	0.7	189	11.5	551
Total input	5	269	86.3	1222
Leaching	1.2	21.3	5.9	240
Runoff	(2)	(81)	(189)	(338)
Crop yield	0.15	10.4	1.4	69.9
Dirt tare	0	0.1	0.2	0.3
Animal produce	0.01	0.46	0.03	15.9
Total output	1.4	32.2	7.5	326
Accumulation	3.6	236.8	78.8	894

Source: Wilcke & Döhler (1995)

For all four metals, accumulation occurs in agricultural soils. Runoff numbers were put between brackets by the authors since this flow does not really change the soil contents. However, this flow may result in a considerable loading of rivers (Wilcke & Döhler, 1995).

Comparison of heavy-metal balances

The heavy-metal balance studies which have been undertaken in the Netherlands illustrate the large uncertainties in quantifying particular flows and the large differences between fertilizer plans and farming systems. On the national scale, the inputs of heavy metals by (transboundary) air pollution, the imports of feed concentrates (containing Cd, Cu, Zn), and P-rock (containing Cd) are striking.

In Denmark, the effects of legislation on decreasing the heavy-metal surplus on the balance is quite positive. The prohibition of Cd in products combined with stack gas cleaning has led to much less emissions in the last few years. Moreover, the Cd contents in P-fertilizers have decreased as well.

The Swedish study shows interesting differences between the four heavy metals in the different regions due to different farming types, application rates of fertilizers and crop offtake characteristics. In some cases, Cu and Zn are even depleted.

In Finland, the low depostion rate of Cd and the exceptionally low Cd input with P-fertilizers (Kemira) has (on average) lead to a steady-state situation (*i.e.*, 'no net

accumulation') for Cd in arable farming. Copper is added in large amounts due to Cu-fertilizers. Manure applications result in large Cu and Zn inputs.
The study on different farming types in Austria reveals large differences between farming types and sometimes even larger variations within these farming types. Local sources (like Cu in piping) may constitute important inputs on single farms, which shows the potential for optimizing heavy-metal balances on this scale.
Estimated heavy-metal balances of German agriculture show a large surplus for all four metals, which are explained by the same processes as in the Dutch situation.
Analysis at the national level gives insight in the position of the agricultural sector with respect to imports and exports. Such an analysis, however, is not sufficient for identification of local problems. Spatial distribution of a surplus plays a major role and may differ substantially per field, farm, province or nation. Therefore, a legitimate question is to which extent aggregated analyses and national balances result in relevant outcomes for environmental analysis and management of agro-ecosystems. The big differences between and within these systems necessitate a specific analysis on the farm scale in order to get insight in different mechanisms and rates of heavy-metal accumulation in different agro-ecosystems. Characteristic flows and processes are in that way recognized. Since management measures will take place directly at farm level as well, such a specific approach offers a way to 'finetuning' heavy-metal management per farming system and even per individual farm.

Environmental management on the farm scale

For control-purposes by the government, the agro-ecosystem may be viewed as a black box for which only the external cycle counts. In order to manage and direct the heavy-metal flows it is necessary to distinguish between several compartments (*e.g.*, soil, crop, animals) and to quantify the internal flows as well (cf. Oenema, 1996). The definition of subsystems recognizes the system's substructure. Control of a system is mostly practised at the subsystem level and seldom by attempting to manipulate the entire system as a single entity. As a system manager, the farmer is the manipulator of subsystem variables and the interaction among subsystems (Rykiel, 1984).
An environmental management system (EMS) is intended to systematically achieve a firm's environmental objectives. The term 'system' shows that environmental management must be applied to all of the company's activities, that measures should be coherent, and that processes should be monitored by way of systematic feedback (Cramer & Glasbergen, 1996). Thus, the aim of an EMS for agricultural firms is to integrate environmental requirements into the full range of agricultural production processes and hence to improve the environmental performance.
Heavy-metal management is the process of decision making with regard to the management of heavy-metal flows. This management process is a cyclic process consisting of analysis, developing options, decision making, execution and control.

Like in farm economic management, it distinguishes between decision making at the strategic, the tactical and the operational level with long-term goals (like farm size and type), choices per growing season and crop rotation (like fertilizer plan) and choices within one day (like sowing and harvesting), respectively (Oenema, 1995). The question is whether it is possible to set up an EMS at the farm-level, thus making environmental aspects an integral part of short-term (operational), middle-term (tactical) and long-term (strategic) decision making. One characteristic of the system's approach is feedback. Thus, the information about the desired and actual output of the system is used to control and guide the input. Therefore, the focal point in environmental management of farms should be at the input side, which requires 'input management' (Odum, 1989).

Beembroek *et al.* (1996) discussed the adjustment of farm accounting to satisfy the demand for environmental data. Bookkeeping of nutrient inputs and outputs at the level of individual farms has already been selected as a new solution to control nutrient use and to tax nutrient surplusses in Dutch agriculture. This mineral accounting system (MINAS) consists of a yearly registration of in- and outputs of N, P and K on the different fields (*i.e.*, field scale) of the farm. This is the most ideal scale since fertilizer applications depend on the crop requirements per field. Also, internal (*e.g.*, roughage and manure) cycles can be accounted for if the field-scale balance is used. Grouping the field-scale balances results in the farm-gate balance. Introduction of a MINAS may strongly affect the choice of fertilizers in a fertilizer plan and may serve to convince and direct farmers to increase their nutrient use efficiency. The MINAS can be coupled with the financial accounting system. Integration of nutrient, heavy-metal and financial accounts is needed to enable auditing at the farm level and to use the accounting systems together as an environmental policy instrument.

If registration of material is implemented in the administrative organisation of a firm it provides insight in the nature, amounts, and throughput of the raw materials, products and waste flows in that firm. Whereas monitoring of soil contents is re-active, monitoring by environmental farm accounting is pro-active since it provides management information. Many data are needed from the trade partners of the farm. In the Netherlands, standard nutrient contents of all the products involved have been established. Of course, data on the real contents are preferable. The invoices should contain the necessary product information, as the invoice is the basis of the accounting process. In the case of organic fertilizers, the delivery voucher can play the role of the invoice (Beembroek *et al.*, 1996). The optimization study by Velthof *et al.* (1996) shows that in order to decrease the total heavy-metal load, it makes sense to introduce a product label for fertilizers, specifying heavy-metal contents. Without such product specification, a farmer cannot compose a fertilizer plan and crop rotation that, as a whole, meets the requirements. By labeling products, farmers can choose and select themselves. This is already put into practice in the Netherlands in the case of certified compost and of feedstuff vouchers that show Cu and Zn contents.

Accumulation of minerals and heavy metals is calculated as the difference between measured and estimated input and output flows. Since all mistakes will add up in the calculated accumulation, reliable data must be gathered and uncertainties should be quantified. The amount which is to be allowed to accumulate on the farm may depend on the current soil quality (heavy-metal content and fertility status). External factors (like weather and soil type) affect the build-up of the surplus also. If external factors dictate the balance, setting a levy on the surplus loses its justification.

According to Udo de Haes & De Snoo (1996), an EMS can be supported by a material approach (*e.g.*, substance and material flow analysis), a product approach (*e.g.*, life cycle analysis), a process approach (*e.g.*, integrated chain management), a region approach (*e.g.*, linkage of material and energy flows), and an actor approach (consumer/producer responsiblity).

Eco-labeling of farming produce is a product policy based on life cycle analysis (LCA). However, the use of LCA is limited due to methodological, financial and organizational problems. A label for all farming produce is impossible and taking the product as a functional unit is only logic from a consumer's point of view (Udo de Haes & De Snoo, 1996).

Company certification may solve the problems that go along with eco-labeling. The farm level is very strategic, because there the farm management is influenced directly and it is relevant for all products that are produced on the particular farm. Company certification needs clear environmental performance indicators on a relevant range of environmental pressures (*e.g.*, heavy metals, nutrients, energy, water, pesticides). The possibilities for introducing company certification depend on legal, administrative and economic consequences. Certification should be voluntary (farmers taking their responsibility) and information based. However, implementing an EMS needs control as well, which raises the question how a proper monitoring and control (auditing) can be established. Choosing the company level may be even more complex than a product approach and does not guarantee that all products from a firm actually deserve a certificate. However, since the full range of company operations is taken into account, problem shifting will be avoided (Udo de Haes & De Snoo, 1996).

Another important question is if company certification can be put in a chain perspective. In a whole-chain management perspective, all actors in the agro-production chain (industry, producers, trade, retailers, consumers) should be involved since sustainable agriculture is a responsibility of society as a whole (Udo de Haes & De Snoo, 1996).

Farmers should develop a sustainable management of agro-ecosystems as reflected in certification of their firms (material approach) and products (product approach). Consumers are responsible for an acceptable income level by paying appropriate prices for these certified products (actor approach). Also, the individual firms obviously cannot control every environmental impact. So, it is necessary to develop integrated chain management in which the different firms that comprise a single product chain join together to obtain cleaner production (process approach).

Knowing the interactions and feedback mechanisms among the different subsystems of the whole production chain, gives insight in the effect of changes in a production system on the emission of contaminants (Lambert, 1994).
Industrial ecology states that companies should optimize the use of energy and material, minimize waste production, and use the effluents of one process as input for another process (Frosch and Gallopoulos, 1989). Thus, by strategic cooperation between industrial, agricultural and recycling firms environmental 'savings' could be realized by 'industrial symbiosis'. Whereas integrated chain management aims at optimizing processes within the production chain, the optimization process might be taken even further *e.g.*, by promoting 'mixed farming' at a regional level (region approach).

Conclusion

Heavy-metal balances on a national scale study the agricultural sector as a whole. Although their meaning is quite limited with regard to environmental analyses, they give valuable information for economic analyses. The studies on heavy-metal balances in Denmark and Finland show that generic measures may be very fruitful. Generic measures at the (inter)national level are required to enable proper procedures and measures with regard to product labeling, company certification, industry convenants, and import and trade with regard to heavy metals.
Whereas the controlling measures that are based on direct economic instruments or generic regulations often ignore farm characteristics and individual management options, field-scale and farm-gate balances give farmers specific feedback on effective options for a better heavy-metal management. Farm-gate balances show the total contaminating potential, whereas field-scale balances enable a direct link with criteria for the protection of soil and other environmental criteria.
Incorporation of heavy-metal balance sheets in an environmental management system of individual firms may result in combining several categories of controlling measures, *i.e.*, information and extension, economic incentives, and legislative measures. Moreover, an environmental management system can be supported by material flow analysis (material approach), life cycle analysis (product approach), integrated chain management (process approach), and by 'mixed farming' at a regional level (region approach).
In Chapter 4, the information that is needed to calculate realistic heavy-metal balance sheets on the field scale of agro-ecosystems is discussed.

CHAPTER 4

BALANCING HEAVY METALS. III. HEAVY-METAL BALANCES OF AGRO-ECOSYSTEMS ON THE FIELD SCALE

Abstract

Whereas heavy-metal balances may be calculated on all spatial scales (*i.e.*, field-, farm-, and national scale), the most appropriate scales for managing heavy-metal flows directly are the field- and farm scales. In this chapter, the information that is needed to calculate heavy-metal balance sheets on the field scale of agro-ecosystems is discussed. The metal behavior in the plough layer determines the resulting heavy-metal fate, *i.e.*, accumulation in the agro-ecosystem's soil, output with produce and output to deeper soil layers and groundwater.

in soils and plants in various ways. Although atmospheric input may be small compared to the total soil pool, the metals are largely retained in the topsoil and may be subsequently taken up from the plough layer of agro-ecosystems. Navarre *et al.* (1980) found that soil contamination in Belgium caused by deposition exceeded the contamination through the use of chemical fertilizers by far for a series of heavy metals. It has to be noted that this resulted from the presence of (non-ferro) metal industries on a relatively small area and that the situation has improved since 1980.
The contribution of dry and wet deposition of heavy metals on the plant surface (*i.e.*, interception) to plant metal levels may also be considerable and may even exceed that of the uptake from soil. The importance of interception of Pb deposition was first appreciated when a mass balance was calculated for Danish soils. When Pb is incorporated into the soil it appears to be immobilized and is not subsequently taken up to any appreciable extent by plants. Percentages as high as 90 or more of the total plant uptake of Pb in plants were due to deposition from the atmosphere rather than transport from the soil (Tjell *et al.*, 1979). Dalenberg & Van Driel (1990) found that direct atmospheric deposition contributed considerably (up to 95%) to Pb concentrations in the leafy material of grass, spinach and carrot, and of wheat grain and straw. The contribution of deposition to the Cd concentrations of these crops was significant only in wheat grain and straw. Mitchell (1974) and Yläranta (1994) showed for Scottish and Finnish soils respectively that most of the Pb in crops is from airborne origin. This is remarkable in the sense that both countries are relatively remote from the centre of economic activities in Europe.
Data needed for the characterization of the interception by food crops are deposition velocities, absorption coefficients, interception fractions, and half lives for the retention of particles on the surfaces of crop plants (Tiller, 1989). Plant based foodstuffs are the largest source of dietary Cd and, therefore, the relative contribution of Cd interception and soil Cd to the Cd content plants is important but as of yet largely unresolved (Johnston & Jones, 1995).
Thus, atmospheric deposition can be a significant source of heavy-metal input to both soils and plants (*i.e.*, the foodchain) in agro-ecosystems, particularly where background soil levels are relatively low (Haygarth & Jones, 1992).

Mineral fertilizers and manure:
Nitrogen (N), phosphorous (P) and potassium (K) are the primary nutrients supplied by mineral and organic fertilizers.
Phosphatic fertilizers represent the largest input of Cd into pastoral farming systems in New Zealand due to the abscence of high Cd deposition rates. Loganathan *et al.* (1995) showed a clear relationship between P-fertilizer use and Cd accumulation, thus providing evidence of the contribution of P-fertilizer to soil Cd. In their Cd balance, they took into account the redistribution of Cd by animal grazing and camping behavior, since animal grazing and excretion patterns influence the redistribution of fertilizer Cd in the pastoral system. Regular, long-term P-fertilizer topdressing has been the major source of Cd in pasture soils of Australia and New

Zealand increasing total soil and herbage Cd (Andrewes *et al.*, 1996).
Animals are exposed to metals in their diets and any heavy metal not retained in the body will be excreted. Where stock are bedded on straw, the farm yard manure will contain additional Cd derived from the bedding. The Cd concentration in such organic wastes may have increased, because herbage and straw used for feed and bedding respectively have been exposed to (atmospheric) contamination (Johnston & Jones, 1995).
Application of heavy-metal containing fertilizers may thus increase metal levels in soils, but increased metal levels in soils do not necessarily result in increased metal contents in the plants grown in the fields. Whether increases in soil and plant metal levels will occur as a result of organic and inorganic fertilizer application depends upon a variety of factors, such as soil properties, metal contents and type of fertilizers, rates and duration of fertilization, and plant species. The pH-metal uptake relationship is dependent on soil types and plant species as well (He & Sing, 1995).

<u>Other inputs:</u>
The input by irrigation and flooding (inundation) depends on the amount of water involved and its concentrations. The concentrations depend on the source of the irrigation water which may be surface water (with higher concentrations due to the presence of particulate matter) and groundwater. Effects on hydrological properties and on the redox status of the soil resulting from these inputs should be accounted for as well (Iimura *et al.*, 1977). Pesticides containing considerable amounts of Cu and Zn are used for certain crops (*e.g.*, potatoes) only. Compost and sewage sludge are location specific inputs that can be taken into account as well. Mineral rock weathering constitutes an input to the subsoil of agro-ecosystems that is mostly greatly exceeded by anthropogenic sources (Ross, 1994).

Outputs (O)
The fate and distribution (internal fluxes and output flows) of heavy metals depend on the farm management (metal input characteristics, the type of land use and farming system), on the prevailing soil properties and conditions, and on the climate and hydrological conditions. Palm (1994) coupled a model for equilibrium sorption to a hydrological model and found that the sorption isotherm influenced Cd transport more than root distribution or hydrological properties of the soil profile. The degree to which heavy metals sorb to soil determines how much will be available in the soil water for plant uptake or transport to the groundwater. The sorption capacity of a soil is highly dependent on its physico-chemical properties, especially pH. Organic matter is known to adsorb considerable amounts of inorganic cations and complexation with dissolved organic carbon may be important as well.
In assessing the long-term behavior of metals in agricultural soils, it is important to take into account which assumptions have been taken as a starting point for the modeling of sorption. With regard to the long-term behavior of heavy metals in soils, the essential point is whether the adsorption can be taken as approximately

constant (linear isotherm) or as a decreasing function of surface coverage (non-linear isotherms). The latter case, which can be approximated by either a Langmuir or a Freundlich adsorption equation, results in a higher solubility of heavy metals with higher accumulated amounts. In the case of Freundlich-type adsorption of heavy metals in soils, eventually all metals that reach the soil would be removed by crop uptake and leaching, similar to the linear case. However, in the linear case, the rates of plant uptake and leaching increase linearly with the soil content, whereas in the non-linear case the rates of leaching and plant uptake initially tend to be lower than in the linear case but eventually increase more steeply (Harmsen, 1992).

Leaching rate (L):
The total amount of heavy-metals in soil (G) is the sum of fixed, adsorbed, and dissolved heavy metals. The fixed fraction of heavy metals cannot be released into the soil solution while the adsorbed amount participates in the equilibrium reactions between the soil solid and solute phases. By measuring adsorption isotherms, the relationship between the heavy-metal concentration in solution (c: g m^{-3}) and the adsorbed amount (q: g kg^{-1}) can be derived assuming that equilibrium is instantaneous and that no desorption hysteresis occurs. Adsorption of a heavy metal can for instance be modeled with the Freundlich sorption equation, given by:

$$q=k_f c^{n} \tag{4.3}$$

where k_f (g^{1-n} $(m^3)^n$ kg^{-1}) and n (-) are constants. Using the Freundlich equation, the labile content G_l (*i.e.*, the sum of the adsorbed amount in the solid phase and the dissolved amount in the soil solution) is expressed as:

$$G_l=\theta c+\rho k_f c^{n} \tag{4.4}$$

Here, θ is the volumetric water content of the soil (m^3 m^{-3}) and ρ is the soil dry bulk density (kg m^{-3}). Commonly, the distribution ratio defined by

$$r_d=\frac{\rho q}{\theta c} \tag{4.5}$$

is large. Hence, θc can be neglected in Eq. 4.5 to obtain an approximation for the relationship between c and G_l:

$$c=[\frac{G_l}{\rho k_f}]^{1/n} \tag{4.6}$$

The leaching rate (L) is the product of precipitation surplus and heavy-metal concentration in solution. Consequently, the leaching rate from the plough layer can be related to the labile fraction of the total soil content (G_l: g m^{-3}) using Eq. 4.6:

$$L = \frac{P_s c}{l_p} = \frac{\theta v c}{l_p} = \frac{\theta v}{l_p}\left[\frac{G_l}{\rho k_f}\right]^{1/n} \tag{4.7}$$

where P_s is the precipitation surplus (m yr^{-1}), v is the pore water velocity (m yr^{-1}), and l_p is the plough layer thickness (m).

Plant uptake rate (U):

The contaminant burden of a crop is usually a combination of interception, surface contamination from adhering soil, and uptake from the soil via the root system. In the field, all processes may operate at the same time (Lexmond, 1992). Hence, correlation between total contents in the soil and concentrations in the plant does not always relate to the way that metals reach the crop. So, root uptake and translocation to (aboveground) edible tissues are important processes in the analysis of metal movement in agro-ecosystems, but the contamination of plant surfaces with soil particles may be an important process in the transport of heavy metals in agro-ecosystems as well. Pinder & McLeod (1988) found that soil retention on grain and leaf surfaces could cause soilborne heavy metals to be incorporated into foods in quantities that exceed those predicted by measures of root uptake. Different factors, such as raindrop splash, wind erosion (saltation), soil disturbance by mechanical equipment and livestock activities may contribute to the amount of soil particles transported from the soil to plant surfaces. This means of transport of heavy metals to foliar surfaces may be of particular concern in soils high in heavy-metal content. Pasture and fodder are not washed before consumption by farm livestock while crops for human consumption are.

The principle processes for transport of metals from soil to plant root are convection (mass flow) and diffusion. Metal ion uptake can be passive (apoplastic) and active (symplastic). The rhizosphere (*i.e.*, soil near the plant roots) can be changed by plant roots through exudation of chelating agents and by changing the soil pH in order to increase the nutrient supply. Crop species and cultivars differ widely in their ability to absorb, accumulate and tolerate heavy metals and they show a range of different mechanisms for protecting themselves against metal uptake. Types of metal tolerance mechanisms in plants include selective uptake of ions, decreased permeability of membranes or other differences in membrane structure and function, immobilisation of ions in roots, foliage and seeds, removal of ions from metabolism by storage in fixed and/or insoluble forms, alteration in metabolic patterns, adaptation to toxic metal replacement of a physiological metal in an enzyme, and release of ions from plants by leaching from foliage, guttation, leaf shedding, and excretion from roots (Kabata-Pendias & Pendias, 1984). In agricultural practice, the distribution of the plant-adsorbed Cd over the different plant parts may be of utter importance. Generally, Cd contents in the root and shoot are related by a simple linear relationship. For maize, Florijn & Van Beusichem (1993) found values for the shoot/root distribution factor varying between 0.4 and 0.04.

It is reasonable to expect crop uptake to be related to the soil solution concentration since that is the plant-accessible fraction of a metal. Gerritse *et al.* (1983) found that log-log plots of concentrations in the plant and the soil solution concentrations showed the best correlation for Cu, Cd, and Zn. For Pb, generally no significant relationship between plant uptake and soil solution concentration or any soil parameter could be found. Novozamsky *et al.* (1993) found a close relationship between the Cd content in vegetables and its concentration in a 0.01 mol l^{-1} $CaCl_2$-extract. However, in soil-crop ecosystems, the relation between the biological availability and the solubility of heavy metals is very complex. Actual uptake of heavy-metal species depends on the concentrations and speciation of the metal in the soil, the movement of the metal from the bulk soil to the root surface, the transport of the metal from the root surface into the root by crossing the membrane of epidermal cells, and its translocation from the root to the shoot (xylem), and possible transport from the leaves to storage tissues normally used as food (seeds, tubers, fruits). Each of these processes strongly affects whether a potential toxic element reaches the food chain, and each process is strongly affected by the chemical speciation of the element. (Alloway, 1990). Thus, reaction kinetics determining the rate of element transfer from solid to liquid phases and to plant roots, in combination with synergistic and antagonistic effects of nutrients and toxic elements, will determine the resulting plant uptake.

Fertilizer additions may affect the uptake of heavy metals. Lorenz *et al.* (1994) found that an excess of fertilizer cations in the soil caused drastic changes in the concentrations in solution of major ions and heavy metals during some stages of their experiment and concluded that fertilizer application to a site contaminated with heavy metals may lead to a temporary mobilization of heavy metals and, therefore, increased bioavailability and danger of toxicity.

Eriksson (1990) found that the total Cd content of the soil and soil pH are the main soil factors influencing the uptake of Cd by plants from Swedish soils. The decline of atmospheric deposition suggests that phosphate fertilizers may become a more prominent source of soil Cd. Johnston & Jones (1995) suggest some differences in the immediate availability of Cd in phosphate fertilizers and atmospheric depositions. He & Sing (1995) found that Cd contents in plant species increased with increasing Cd content in the fertilizers, except phospate rock, in which Cd was not easily available to plants.

Poelstra *et al.* (1979) studied adsorption and uptake of Cd in different plants as a way of estimating the influence of applicating sewage sludge for different types of soil. They introduced an uptake selectivity coefficient, which was defined for each type of crop as the ratio between the actual uptake of an element and the uptake which can be calculated from the amount of water taken up by the plant times the concentration of that element in that water. They found that their simplified model was still too complex to use it for a quantitative evaluation of most of the literature on Cd uptake.

A deterministic model for Cd uptake from soils has been developed by Christensen & Tjell (1984). It divides the total plant Cd into three source-based fractions, *i.e.*, Cd from the atmosphere, Cd from the topsoil, and Cd from the subsoil. This model predicts the plant Cd response curve to consist of a base line contribution originating from air and subsoil uptake superimposed by a contribution from topsoil uptake. The topsoil concentration is affected by soil amendments and is therefore variable. This model is conceptually very elegant, but could not be tested sufficiently.

Lindstrom *et al.* (1991) and Boersma *et al.* (1991) developed and tested a detailed mathematical model of plant uptake and translocation of organic chemicals that was formulated by defining a generic plant as a set of adjacent compartments representing the major pools involved in transport and accumulation of water and solutes. Although their concept of plant uptake and in-plant transport is well-defined it requires information on anatomical dimensions and physical and chemical coefficients that is not available.

Hooda *et al.* (1997) found that the plant availability of heavy metals grown on soils from 13 sites previously amended with sewage sludge differed widely among the crop species studied. Multiple regression analysis of various soil properties showed that the soil metal content was the principal factor controlling metal contents in the plants, and was the only factor which consistently appeared in all models. Thus, they concluded that the most certain way to control the accumulation of metals in food plants is by controlling soil contents.

Hence, an alternative to deriving relationships between solute concentration, transpiration rate and plant uptake is to consider the plant uptake as being proportional to the labile metal content. Therefore, although there are many soil and plant factors that influence heavy-metal availability to plants, crop uptake is expressed here according to the relationship

$$U = B G_l^m \tag{4.8}$$

(cf. Kuboi *et al.*, 1986). Here, the value of m (-) depends on the uptake behavior and the plant uptake rate coefficient, B (yr^{-1}), can be related to the crop yield (Y: kg m^{-2} yr^{-1} DW), the metal content in the crop (c_p: (mg kg^{-1} DW), and the labile soil content according to:

$$B = \frac{Y c_p}{l_p G_l} \tag{4.9}$$

In Eq. 4.9, it is assumed that metal uptake is limited to the plough layer. Other factors that influence the burdening of plants with heavy metals (*e.g.*, interception) could be incorporated in Eq. 4.9 as well.

Competition:

Contamination of soil by single heavy metals has been studied extensively, but little is known on the effects of combinations of heavy metals on their adsorption and consequent mobility and availability (*e.g.*, synergism or antagonism). The adsorption capacity of the soil could be exhausted earlier than expected due to competition effects between cations (*e.g.*, Schmitt & Sticher, 1986). If adsorption and pot or column experiments are carried out with a combination of different metals, a more realistic expression for the resulting solute concentration and subsequent uptake and leaching characteristics may be derived.

Soil-bound heavy-metal output flows:

The losses through soil-bound heavy-metal flows like dirt tare, runoff and wind erosion may be a significant burden to other environmental compartments. In the SB and DB approaches, the heavy metals that are leaving the system as 'soil-bound' flows are regarded as regular output flows. However, the (surplus on the) balance sheet also depends on effects of the metal flows on soil level and composition. Discriminating between output flows that are soil-bound and output flows that are not complicates the calculations considerably, because the matrix of heavy-metal carriers is to be taken into account properly. In order to solve these complications, Moolenaar *et al.* (1997b) developed the 'dynamic soil composition' balance (DSCB) approach. This approach is explained and elaborated upon in Chapter 5.

The dynamic balance of the topsoil:

A differential equation represents continuous changes of state with time and by substituting Eqs. 4.7 and 4.8 in Eq. 4.2, a differential equation develops in terms of (labile) heavy-metal content in the topsoil:

$$\frac{dG}{dt} = A - BG_l^m - CG_l^{1/n} \tag{4.10}$$

in which the leaching rate parameter (C) is given by:

$$C = \frac{\theta v}{l_p}\left[\frac{1}{\rho k_f}\right]^{1/n} \tag{4.11}$$

Analytical solutions are available for particular values of m and n, whereas for other cases the solution of Eq. 4.10 must be approximated numerically (cf. Boekhold & Van der Zee, 1991).

The rate paramaters (A, B, C) are lumped *i.e.*, within certain spatial and temporal limits, they are considered as constants. These rate parameters are a function of soil and management characteristics and they can be derived from measurements or estimations for any agro-ecosystem. With the dynamic balance (Eq. 4.10) soil contents can be calculated as a function of time, revealing if problems are likely to occur and, if so, for which element, in which compartment (produce or groundwater) and on which time-scale.

Aggregation

There certainly is a need for basic research on low spatial scales. However, results need to be related to higher spatial scales in order to answer questions that are often being raised from a policy and management point of view. Environmental management on the regional scale demands consideration of soil processes and resulting fluxes that occur on that scale. The ability to directly use process-level information from geographically smaller (*e.g.*, field) scales to do this is at all ways problematic, and at times clearly in error. On the regional scale, there is very little opportunity to directly observe and quantitate the myriad processes and their combinations that influence the water and chemical fluxes on lower scales. The methodology of scale translation therefore demands careful consideration. 'Down-scaling' is used for decomposing process information (*e.g.*, remotely sensed data) from the higher level to the lower (*i.e.*, top-down) and 'up-scaling' (*i.e.*, aggregation) studies use results from a smaller spatial scale to improve the understanding and of processes on the regional scale (*i.e.*, bottom-up) (Wagenet, 1996).
An aggregate is a group of entities in which one or more of these entities do not have any relationship with the whole group of entities whatsoever. Aggregation may thus be defined as putting parts or systems together without their being necessarily related or dependent (Kramer & De Smit, 1987). Consequences of the use of aggregated units are often not explicitly analyzed, although this may lead to considerable errors (*e.g.*, CFEM, 1996b).
The input and output rates in the balance equation (4.10) are a function of soil and management characteristics, which can be derived for fields of a specific farm. For aggregation purposes, the question is how information about these soil characteristics and qualities may be properly translated across different spatial and temporal scales. With regard to the temporal scale, it is impossible to choose a time-base to suit the rates of all processes. Thus, the chosen timebase to model the dynamic behavior of soil processes may be one day (crop growth models) one year (*i.e.*, growing season) or one crop rotation.
Heterogeneity of the fields expressed as the statistical variation of soil parameters within the system under investigation is neglected in our approach and the field-scale analyses may thus be aggregated to a larger scale if it is assumed that the fields studied are representative for the farm, that the farm studied is representative for a specific farm-type, and that the farm-type represents a certain percentage of the

agricultural sector in that region. This approach would result in application of a generic data set to a whole region.

It is possible to reasonably estimate the input rate in different systems based on fertilizer-, feedstuff- and soil use (*e.g.*, crop rotation). The values of the crop uptake and leaching rates, however, are very site specific and depend on a combination of soil characteristics and farm management. This complicates the aggregation of results on field scale to farm and regional scales and thus aggregation of field-scale (both SB and D(SC)B) models can only be carried out if an extended database were available with distribution functions of the relevant input and output rates.

Geographic information systems (GIS) enable an integrated assessment of environmental issues and if the parameters in GIS could be combined in such a way that these input and output rates were known, large-scale assessments might become possible. In that case, soils should be grouped according to their buffering capacity for heavy metals and the loads on these soils should be combined with these groups. However, the parameters stored in GIS are not sufficient to enable aggregation, since they consist of the less variable soil characteristics (like the soil profile and the estimated texture, carbonate- and organic matter content). Essential parameters like the pH-value and farm management information are not stored in GIS. Large-scale process analysis (*i.e.*, qualitative, conceptual) may override or average out the effects on the local scale since large-scale models often use 'lumped' parameters which subsume much of the process-level complexity of lower scale analysis (*i.e.*, quantitative, mechanistic). In order to improve on scale translations, an appreciation of scale dependency is needed first and furthermore measurement and monitoring approaches should be consistent in scale with the modeling approaches on the regional scale. With a large-scale analysis, a dynamic (long-term) assessment is impossible at the moment due to lack of the required data. For large-scale, static (one year) assessments existing national bookkeeping systems can be used.

For the moment, the top-down and bottom-up results could be used in a complementary way. With the one general trends are discovered and with the other site and farming system specific investigations can be carried out. Different possibilities to assess heavy-metal balances are presented in Table 4.1.

Table 4.1. Different possibilities for assessing heavy-metal balances.

	Static (one-year):	Dynamic (long-term):
Top-Down:	- national bookkeeping system	- not available
Bottom-Up: (small-scale)	- farm-gate balance & SB - bookkeeping system	- field-scale balance (DB or DSCB)
Bottom-Up: (large-scale)	- bookkeeping system (aggregated field/farm results)	- not available - GIS+DB/DSCB?

SB: static balance; DB: dynamic balance; DSCB: dynamic soil composition balance; GIS: geographical information system

Conclusion

In order to determine the options for a sustainable heavy-metal management in agriculture, heavy-metal balance sheets are used. These balance sheets are a means to quantify heavy-metal (input and output) flows, resulting accumulation, and associated risks. Heavy-metal flows in agro-ecosystems may be studied within the broader context of substance flow analysis and industrial ecology. Since heavy-metal balances may be obtained for different farming systems in different countries for different spatial scales, the choice of the scale of analysis is a very important one. If a certain scale has been chosen, a consistent approach is needed to reveal the consequences of heavy-metal flows within the defined system by quantification of flows, data presentation and interpretation of the balance in view of sustainability (Chapter 2).

Balance studies which study the agricultural sector as a whole (*i.e.*, national scale) give valuable information for economic analyses. However, their meaning is quite limited with regard to environmental and specific on-site management analyses. In order to be able to discover relevant options for an effective heavy-metal management of agro-ecosystems, heavy-metal balances on the farm and field scales should therefore be used in addition. These heavy-metal balances could be incorporated in an environmental management system of individual firms (Chapter 3).

In this chapter, the information which is needed to calculate dynamic heavy-metal balances for the plough layer is shown. Moreover, the (im)possibilities to aggregate results on the field scale to higher levels of analysis are discussed. The different approaches to assessing heavy-metal balances (*i.e.*, top-down and bottom-up) may be used in a complementary way. With the one general trends are discovered and with the other field and farm specific investigations are carried out.

CHAPTER 5

CALCULATING HEAVY-METAL ACCUMULATION IN SOIL: A COMPARISON OF METHODS ILLUSTRATED BY A CASE-STUDY ON COMPOST APPLICATION

Abstract

Accumulation of heavy metals in agricultural soil can be prevented by achieving an input that is smaller than, or equal to, the output. This is known as the 'balance approach'. Heavy-metal balance sheets can be used to determine the contribution of different input and output flows to the resulting accumulation. The change in heavy-metal content in the plough layer is the result of the net difference between input and output flows per unit time. Existing balance approaches lack an analysis of the effect of soil amendments on soil composition. However, soil composition determines soil bulk density and plough layer weight and hence the resulting change in heavy-metal content. It is therefore important to understand and account for the processes that affect soil composition. Recycling of compost produced from source-separated organic household waste as a soil amendment in agriculture is used as an example to illustrate how changes in soil composition complicate accumulation calculations. The dynamic soil composition balance approach is presented as a way to handle these complications by calculating mass balances of both heavy metals and main soil constituents.

Comparing results of the dynamic soil composition balance with those of other balance approaches reveals the necessity to account for changes in soil composition and for the effect of soil-bound heavy-metal flows in calculating heavy-metal accumulation in agricultural soil. This new balance approach is of special relevance if organic soil amendments (*e.g.*, manure and compost) and soil-bound heavy-metal flows (*e.g.*, erosion) are involved.

Introduction

Heavy metals are generally regarded as contaminants, although some are micronutrients for which depletion should be avoided. Their accumulation in soil may lead to increased plant uptake and leaching to the groundwater. Heavy-metal balance sheets are useful to anticipate depletion and accumulation of metals. A proper systems analysis using heavy-metal balances requires that firstly the relevant input and output flows are identified and defined, secondly reliable data are gathered, and thirdly the heavy-metal flows (and their resulting accumulation) are calculated correctly. If these requirements are met, an agro-ecosystem may be judged by the sustainability of its heavy-metal management (Chapters 2 & 3).

In calculating heavy-metal balances, the input (I) and output (O) flows of an agro-ecosystem are compared and their relative influence assessed. In the static balance (SB) approach, the output flows are regarded not to be related to the metal content in the soil and the soil composition is assumed to remain constant in time. Calculating static balances for one year or a single crop rotation evolved in the mid-eighties and has resulted in some interesting publications in the field of heavy-metal balance studies (*e.g.*, Breimer & Smilde, 1986; Smilde 1989; Van Driel & Smilde, 1990). However, because the SB-approach does not consider the dependency between the state variable (content) and output fluxes it cannot realistically simulate the development of the heavy-metal soil content in time (G(t)).

In the dynamic balance (DB) approach, heavy-metal accumulation in the plough layer is the result of the net difference between (the dynamically related) input and output flows per unit time. In DB-approaches developed so far, soil composition, soil bulk density and plough layer weight remain constant (the SB- and DB-approaches are discussed in Chapter 4).

The effects of the matrix in which the heavy metals are added to the soil on soil composition are not accounted for in the SB- and DB-approaches. This chapter presents the dynamic soil composition balance (DSCB) approach, which accounts for the changing soil composition by calculating both a mass balance of heavy metals and a mass balance of the main soil constituents. This may lead to changes in soil bulk density and plough layer weight that affect the resulting heavy-metal content.

An example in which the addition of constituents other than heavy metals has to be considered is the recycling of compost produced from source-separated organic (SSO) household waste, *i.e.*, kitchen waste, residual food and yard trimmings. In the Netherlands, SSO-waste is composted. Agriculture is a potential market for the SSO-compost to improve physical soil characteristics (organic matter status, soil structure and water holding capacity). SSO-compost also has some value as a fertilizer and may raise soil pH. Addition of SSO-compost may cause heavy-metal accumulation because of contamination of compost by heavy metals (TCB, 1991; Fricke & Vogtmann, 1994; Richard & Woodburry, 1994; Deportes *et al.*, 1995). A Dutch General Administrative Order (GAO) of 1991 set limit values for the maximum heavy-metal contents in compost and in the receiving soil, and for the maximum application rates.

Dutch SSO-compost contains approximately 70% dry matter, comprising 30% (expressed on dry weight: DW) organic matter and 70% (DW) soil minerals. In the SB- and DB-approaches, the heavy-metal content changes linearly with compost additions without taking into account the soil that is added at the same time. The Dutch GAO of 1991 (Anonymous, 1991b) accounted for the soil applied in compost by calculating a 'basic load'. This basic load equals that part of the heavy-metal input that does not constitute an additional 'burden' because the mass ratio of heavy metal to soil material in compost does not exceed the soil content. This approach does not account for changes in soil composition.

The DSCB-approach explicitly accounts for the gradual changes in soil composition in the plough layer as a result of the inputs of soil minerals and organic matter. Thus, the changes in heavy-metal contents are related to the changes in solid phase composition, such as the clay, non-clay, and organic matter fractions, as these constituents are chemically relevant.

Besides the input of soil material and organic matter dynamics, changes in the soil surface level after repeated compost additions are taken into account in the DSCB-approach, because SSO-compost applications may result in a small yet significant rise of the soil surface level. An example from the past, where repeated additions of organic fertilizers in fact resulted in a rising soil surface level, is the eutrophic peat area of Central Holland. For several centuries a special manuring method known as 'toemaken' was employed. Dredgings from polder ditches, canals and lakes were mixed with stable manure and spread over the land (ca. 40 ton ha^{-1} every 4 years). In a considerable part of this area the 'toemaak' mixture contained sand and a recognizable anthropogenic A1-horizon developed (Lexmond *et al.*, 1987). Another example is the formation of the so-called 'plaggen' soils in the sandy areas of northwestern Europe from centuries of adding soil-containing manure on arable land. As a result, soils were both fertilized and gradually raised (4 millimetres every 3 years) at the same time (De Bakker, 1979). Application of SSO-compost also involves the addition of significant quantities of soil. Because the plough layer thickness is constant, correction has to be made for the increasing soil surface level.

This chapter develops the DSCB-approach and compares the results with the SB- and DB-approaches. Compost applications are used as an example to illustrate the significance of the differences among the approaches. Moreover, it will be shown how the effect of soil-bound heavy-metal flows like runoff, wind erosion and removal with soil adhering to harvested roots or tubers (*i.e.*, 'dirt tare') on the accumulation of heavy metals in soil can be evaluated according to the DSCB-approach.

Methodology

The total content of heavy metals is calculated with the mass balances for heavy metals, organic matter and other soil constituents (clay, sand and silt) in the plough layer. The organic matter dynamics have to be taken into account in the organic matter balance. The soil bulk density is based on the resulting organic matter content. Corrections based on the soil surface level influence the mass balances directly.

Heavy-metal balance

The balance equation used for assessing the change in heavy-metal content in the plough layer is given by Eqs. 4.1 and 4.2. The dynamic balance equation can be derived in terms of heavy-metal content as was shown in Eq. 4.10. As the sequel to this chapter neglects crop offtake and leaching, the solution to Eq. 4.10 can be simplified to

$$G(t) = G(0) + At \qquad (5.1)$$

where G is expressed in g m^{-2}.

Furthermore, only the heavy-metal input by SSO-additions is accounted for because the focus is on the dynamics of soil composition here. In a more realistic scenario, the contribution of all relevant heavy-metal in- and output flows should be taken into account.

Organic matter dynamics

The dynamics in soil composition are reflected in changing organic matter, clay and non-clay fractions. These fractions determine the soil bulk density and hence the plough layer weight. In the DSCB calculation the organic matter dynamics are modelled according to the 'apparent initial age' concept of Janssen (1984), because this model has proved a useful and accurate tool for simulating organic matter dynamics. Organic matter (Y: kg) decomposition in soil is assumed to follow first order kinetics, according to:

$$\frac{dY}{dt} = -kY; \qquad Y(t) = Y(0)e^{-kt} \qquad (5.2)$$

In earlier models, a constant decomposition rate (k: yr^{-1}) was used. Janssen (1984) determined empirically a time-dependent k for different organic materials because the heterogeneous nature of the organic materials causes the residual to become more resistent during decomposition. This results in a decreasing k-value in the course of time, according to:

$$\log(k) = \log 2.82 - 1.6 \log t; \quad k(t) = 2.82 t^{-1.6} \qquad (5.3)$$

Because this equation cannot be solved at t=0, an 'apparent initial age' (a: yr) was assigned to each type of organic material. Then Eq. 5.3 changes into:

$$k(t) = 2.82(a+t)^{-1.6}; \qquad k(\infty) = 0 \tag{5.4}$$

where parameter 'a' is a measure for the stability of fresh and residual organic matter. Omitting details provided by Janssen (1984), the combination of Eqs. 5.2 and 5.4 yields (after integration and rearranging) an expression for the amount of organic matter Y (kg) at t=t given by:

$$Y(t) = Y(0)e^{(4.7[(a+t)^{-0.6} - a^{-0.6}])} \tag{5.5}$$

In Eq. 5.5, Y(0) is either the amount (in kg) of added organic matter at t=0 or the amount of organic matter present initially. With Eq. 5.5, the build-up of organic matter in the plough layer from regular applications of organic materials (amount Y(0)) can be calculated. Some parameters which might be of relevance, including pH and clay percentage, are not incorporated in this equation. A higher clay fraction may lead to slower organic matter decomposition, because the organic matter can become 'locked up' in aggregates (Hassink, 1995). Nevertheless, Eq. 5.5 has proved very useful in agricultural research for a wide range of soil types and a wide range of organic materials to simulate 'short-term' (20 years) dynamics of added organic matter dynamics accurately and long-term (>20 years) dynamics of soil organic matter quite accurately (Yang, 1996).
It is not realistic to expect that the value of k(∞) becomes zero, because that would result in overestimating the build-up of organic matter. Based on the results of long-term experiments on organic matter decomposition rates in England (Jenkinson & Rayner, 1977), a lower limit of k of 0.003 instead of 0 appears to be more realistic. Then, the adjusted k-value (k') becomes:

$$k'(t) = (2.82 - 0.003a^{1.6})(a+t)^{-1.6} + 0.003; \; k'(\infty) = 0.003 \tag{5.6}$$

Consequently, an adjusted form of Eq. 5.5 has to be used to simulate the organic matter dynamics in our calculations. Equation 5.7 shows that Y(t) then equals

$$Y(t) = Y(0)e^{[(4.7 - 0.005a^{1.6})(a+t)^{-0.6} - (4.7 - 0.005a^{1.6})a^{-0.6} - 0.003t]} \tag{5.7}$$

Soil surface level

In the DSCB-approach, the soil surface level rises slowly, but the plough layer is kept at a constant thickness. As a result, a small part of the heavy metals is 'lost' from the plough layer to the deeper soil layers as mixing by ploughing is limited to *e.g.*, 0.25 m. Therefore, the DSCB-model has a correction factor (*r*) for the 'increa-

sing' soil level and constant plough layer thickness. Some processes, like decomposition of organic matter, losses through dirt tare, runoff and wind erosion can reduce this increase in level or even result in a net decrease of the soil level. These processes are accounted for by using r (a detailed description of r is given in the appendix).
The calculation of the resulting heavy-metal contents is based on the mass balance of all relevant soil components in the plough layer, including organic matter dynamics and compensation for the changing soil level.

Soil-bound heavy-metal output flows
The significance of losses through soil-bound heavy-metal flows like dirt tare, runoff and wind erosion is worth studying, because correcting for these flows in balance calculations may have consequences for the resulting accumulation in the plough layer. In the DB-approach, the heavy metals leaving the system as 'soil-bound' flows are regarded as regular output flows. This can be accounted for by adding an extra term in Eq. 5.1 righthandside, equal to -DG.
Here, D is the amount of soil disappearing by erosion or as dirt tare (kg m^{-2} yr^{-1}) and DG is the amount of heavy metals leaving the plough layer as a part of the soil flows (g m^{-2} yr^{-1}). This amount is assumed to be linearly related to the soil losses.
In the DSCB-approach, however, the soil-bound output flows are not specifically incorporated in the balance equation, but are dealt with by the correction factor r (for changing plough layer thickness) instead. This means that the DSCB-model discriminates between output flows that are soil-bound and output flows that are not.

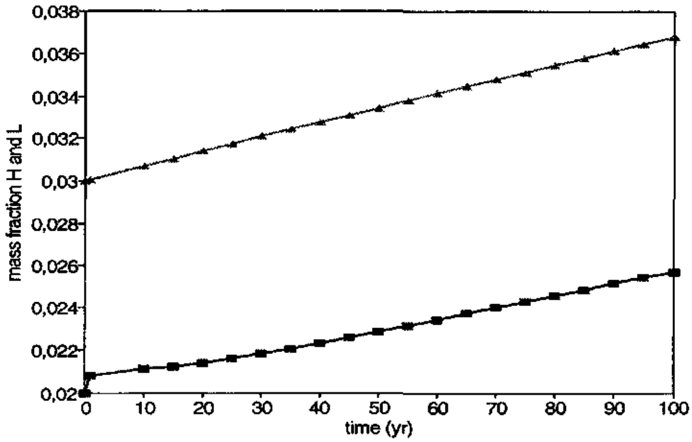
Results and discussion

This section presents the results of the different approaches to calculating heavy-metal accumulation in the plough-layer by comparing the development of the total Cd and Zn contents in a sandy and a loam soil as a result of annual SSO-compost applications of 6 ton (DW) ha^{-1} yr^{-1} (*i.e.*, 0.6 kg (DW) m^{-2} yr^{-1}), which is the maximum permitted rate of application in Dutch farming systems. The Cd and Zn contents in the compost respectively are 0.7 and 150 mg kg^{-1} (DW). The initial values for the Cd and Zn contents in soil respectively are 0.4 and 85 mg kg^{-1} (DW) for the loam soil and 0.25 and 30 mg kg^{-1} (DW) for the sandy soil. The initial mass fractions of organic matter and clay respectively are 0.025 and 0.25 for the loam soil and 0.02 and 0.03 for the sandy soil.
The decomposition rate of organic matter depends on several parameters including the type and age of organic material, and soil type and properties. In the model calculations, the amount of organic matter present at t=0 has an apparent initial age of a=20 for the sandy soil and a=25 for the loam soil. Organic matter accumulates after t=0 by repeated additions of crop residues (a=1.3) and SSO-compost (a=5.5).

Soil composition and reference values

Figure 5.1 shows the changes in the mass fractions clay (L) and organic matter (H) of both soils according to the DSCB-approach. These parameters appear to change significantly within a time scale that is relevant for assessing sustainability (100 yr).

(a)



(b)

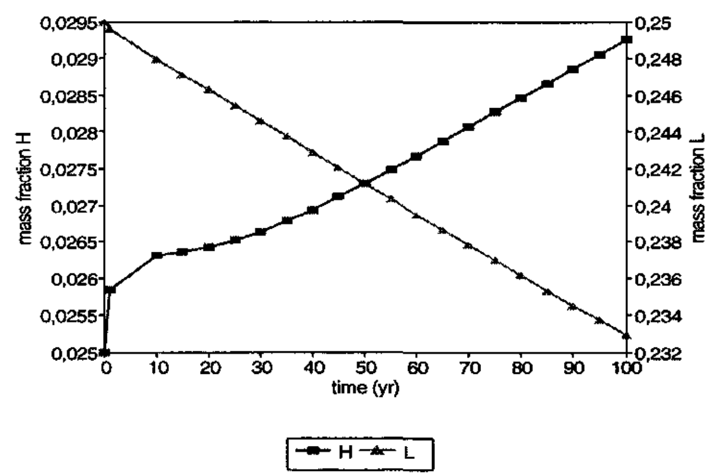


Figure 5.1. Changes in mass fractions clay (L) and organic matter (H) in a sandy soil (a) and a loam soil (b) for annual compost applications of 0.6 kg (DW) m^{-2} yr^{-1}.

The soil bulk density is directly related to the mass fraction organic matter. Increasing this fraction results in decreasing soil bulk density values because the organic matter itself has a lower density than mineral soil particles and organic matter increases soil porosity. As a result of the annual compost applications the bulk density of the sandy soil decreases from 1515 to 1477 (kg m^{-3}) and of the loam soil from 1481 to 1454 (kg m^{-3}), according to the DSCB-approach.

The Dutch 'reference values for good soil quality' (Lexmond & Edelman, 1987), which serve as limit values for heavy-metal contents in soil, are linearly related to a weighted sum of the mass fractions clay (L) and organic matter (H). Thus, these limit values have a build-in soil type correction (Table 5.1). Therefore, the changes in L and H directly affect the limit values.

Table 5.1. Dutch reference values for metal contents in soil (mg kg^{-1} (DW)). Mass fractions clay (L) and organic matter (H) are both expressed in % (w/w) on the dry soil.

	Reference Value
Zn	50 + 1.5(2L+H)
Cd	0.4 + 0.007(L+3H)
Cu	15 + 0.6(L+H)
Pb	50 + L + H

The limit values that are calculated according to the DSCB-approach vary in time as they depend on L and H. The limit values according to the SB- and DB-approaches remain constant at their initial values. Table 5.2 illustrates this for Cd and Zn.

Table 5.2. Development of the reference value for the Cd and Zn contents (mg kg^{-1} (DW)) in a sandy and a loam soil for annual compost applications of 0.6 kg (DW) m^{-2} yr^{-1}.

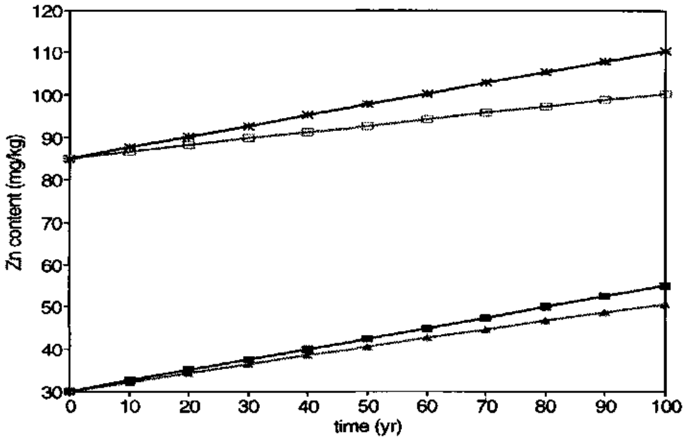
	initial value	after 100 years	difference
Cd-loam	0.63	0.62	decrease
Zn-loam	129	124	decrease
Cd-sand	0.46	0.48	increase
Zn-sand	62	65	increase

The limit value for Cd is very sensitive to changes in H and the limit value for Zn is sensitive to changes in L (see Table 5.1). Therefore, it is important to make an accurate calculation of the mass fractions organic matter and clay over the course of time.

Heavy-metal contents

As an illustration of the relevance of the different concepts, a comparison is first made of the SB-, DB-, and DSCB-approaches. Because crop uptake and leaching are not accounted for and thus only the input by compost is considered, the results for the SB- and DB-approaches are exactly the same and will be referred to by SB.

(a)



(b)

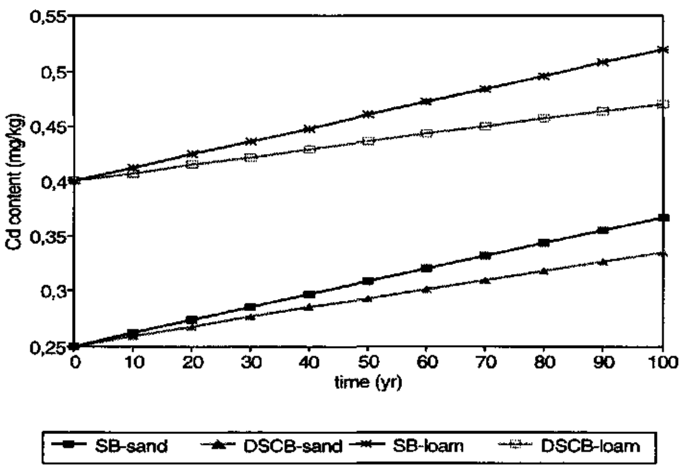


Figure 5.2. Development of the Zn (a) and Cd (b) contents (mg kg^{-1} (DW)) in a sandy and a loam soil for annual compost applications of 0.6 kg (DW) m^{-2} yr^{-1}, according to the SB- and DSCB-approaches.

Figure 5.2 shows that the DSCB-approach results in the lowest heavy-metal contents, as a result of accounting for the changing soil composition and correcting for the changing soil surface level.

The accumulation pattern also depends on the quantity of heavy metals initially present in the soil. If the amount of heavy metals that is 'lost' to the soil layer beneath the plough layer exceeds the amount that is added by compost applications, the soil content will decrease. This occurs in the first year on the loam soil, which has higher initial metal contents than the sandy soil. So, according to the DSCB-approach it depends on the amount of metals added with compost and the total amount that is initially present in the soil, whether the correction factor results in a net increase or decrease of the total amount of heavy metals in the plough layer. However, although the total amount per unit area (g m^{-2}) decreases at first, the total amount per unit mass (mg kg^{-1}) increases. This arises because the total content in soil is calculated by dividing total amounts per unit area by the plough layer weight (kg m^{-2}). The soil bulk density and thus the plough layer weight decrease over time and therefore the total content (per unit mass) increases.
Because of regular SSO-compost applications, the mass fractions clay and organic matter change, resulting in different development paths of the reference values over time. A 'filling-up index' (FUI) is defined as the quotient of the total soil content and the limit (*i.e.*, reference) value. If this index reaches 1, the limit value has been reached. The rate at which the FUI reaches 1 thus shows the rate at which the limit value is being reached, which is an indication of the impact on soil quality. Calculation of these FUI-values with the different balance approaches results in the lowest values for the DSCB-approach (Table 5.3).

Table 5.3. Development of the filling-up index (FUI) for Cd and Zn on a sandy and a loam soil according to the SB- and DSCB-approaches.

	initial value	SB after 100 years	DSCB after 100 years
Cd-loam	0.64	0.83	0.75
Zn-loam	0.66	0.86	0.80
Cd-sand	0.54	0.79	0.70
Zn-sand	0.48	0.89	0.78

Long-term extrapolation
If the heavy-metal accumulation is calculated during periods longer than 100 years, another important difference between the balance approaches is found. According to the SB, accumulation would continue linearly if compost applications are continued. However, the DSCB-calculations show a development towards a certain steady state (Figures 5.3-5.5). Of course, the time-span of 3000 years is not chosen as a basis for realistic extrapolation of calculations. However, it shows the expected patterns of development of the mass fractions of heavy-metal, clay and organic matter towards the steady state. The steady-state fractions of organic matter and clay and the resulting soil bulk densities are the same for both soil types (Fig. 5.3), because the soil composition becomes independent of the initial composition. At steady state, the two soil types will be the same because of long-term SSO-compost applications as a result of the composition of such a 'compost plough layer' being dependent only on the composition of the added compost.

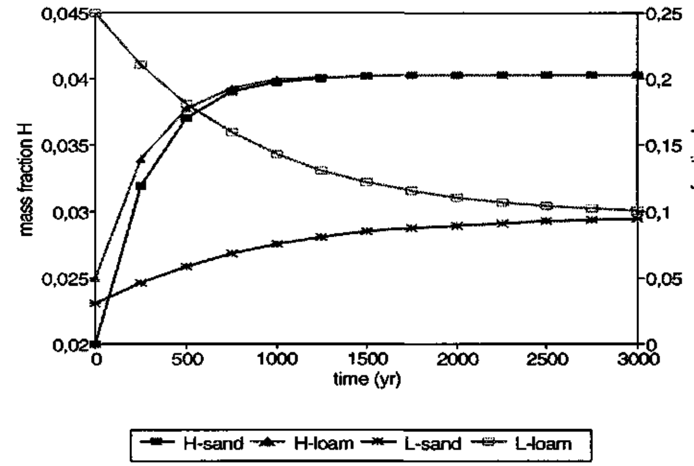


Figure 5.3. Development of the mass fractions organic matter (H) and clay (L) in a loam and a sandy soil.

The heavy-metal contents also increase towards a maximum value at steady state, which is equal for the loam soil and for the sandy soil (Fig.5.4).

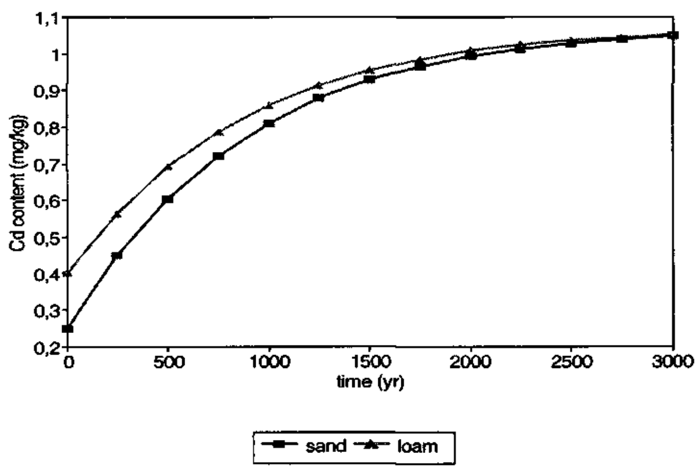


Figure 5.4. Development of the Cd content (mg kg^{-1} (DW)) in a loam and a sandy soil.

The FUI at steady state is the same for the same metals on different soils as well. The maximum FUI-values for Cd and Zn are 1.9 and 2.6 respectively. This means that (independent of the initial soil contents and composition) both metals will exceed the limit values in the long term (Fig. 5.5). Of course, these findings depend on the compost quality.

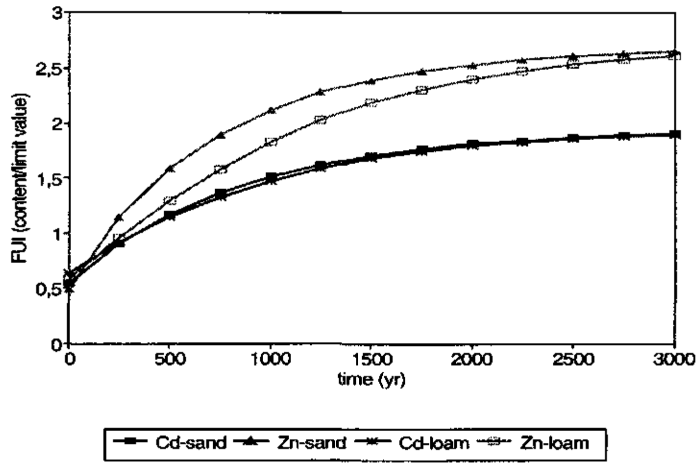


Figure 5.5. Development of FUI-values for Cd and Zn in a loam and a sandy soil.

Another interesting aspect is the outcome of these calculations if the compost load is doubled. The conventional balance approaches (SB and DB) simply assume that accumulation is proportionally related to the amount of compost applied. This is not the case for the DSCB-calculations. Because of the higher application rate the build-up of organic matter occurs faster and stabilizes at a higher level, which results in a lower value for the steady-state soil bulk density. As a result of the correction factor (r), the (steady-state) metal contents (mg m^{-2}) are lower and also reached sooner. However, because of the lower soil bulk density (kg m^{-3}) , the resulting total content in soil (mg kg^{-1}) is about the same for these two application rates, according to the DSCB-approach (Table 5.4). Based on these calculations, the conclusion is justified that higher application rates result in higher fractions organic matter and comparable metal contents and FUI-values at steady state. However, in view of the many uncertainties involved it is impossible to accurately predict the long-term development of the soil composition and the associated heavy-metal contents. If SSO-compost were applied for centuries, the properties of the compost would determine the final heavy-metal contents and FUI-values.

Table 5.4. Comparison of the steady-state situation for SSO-compost application rates of 0.6 and 1.2 kg (DW) m^{-2} yr^{-1} for both a loam and a sandy soil.

	0.6 kg		1.2 kg	
	Cd	Zn	Cd	Zn
Organic matter (%)	4		6.3	
Soil bulk density	1388		1269	
Soil content	1.05	225	1.04	223
Reference value	0.55	86	0.60	87.5
FUI	1.9	2.6	1.7	2.5

Soil-bound flows

If the soil-bound heavy-metal output flows are taken into consideration, a value of D has to be defined. To compare the effect of the size of the soil-bound output flows on the resulting Cd accumulation according to the DB- and the DSCB-approaches, the value of D has been varied between 0 and 2 (kg (DW) m^{-2} yr^{-1}). The present comparison uses two farming systems which are practised on the same loam soil as described above. In case I, only SSO-compost (0.6 kg (DW) m^{-2} yr^{-1}) is added without additional fertilization and associated additional Cd input. In case II, only mineral fertilizers are used and in the DSCB-calculations the contribution of the crop residues to the organic matter content is the same as in case I: 0.36 kg (DW) m^{-2} yr^{-1}. The total Cd input (A) by applying compost and mineral fertilizer is equal in both cases: 0.44 mg m^{-2} yr^{-1}. Table 5.5 shows the resulting accumulation after 3000 years for these different cases.

Table 5.5. Cd contents (mg kg^{-1} (DW)) and FUI-values after 3000 years in a loam soil according to the DB- and DSCB-approaches with different values for the soil-bound flows D (kg (DW m^{-2} yr^{-1}) and different fertilizer plans (I and II).

	D=0		D=1		D=2	
	content	FUI	content	FUI	contents	FUI
DB:						
I	3.97	6.3	0.72	1.15	0.5	0.80
II	3.97	6.3	0.72	1.15	0.5	0.80
steady state: no			app. 2300 yr		app. 1150 yr	
DSCB:						
I	1.05	1.9	1.05	1.9	1.05	1.9
steady state: after app. 3000 yr						
II	3.73	6.3	3.73	6.3	3.73	6.3
steady state: not for heavy metals, but after app. 1500 yr for organic matter						

According to the DB-approach, it does not matter in what matrix the heavy metals are added to the soil. Case I and II consequently result in the same Cd contents despite the different matrices of mineral fertilizer (II) and SSO-compost (I).

The soil-bound heavy-metal flows are explicitly accounted for in the balance equation of the DB-approach as they serve as regular balance posts. Because there is no correction for changing soil composition in the DB-approach, there is no distinction between flows that are related to soil particles and flows that are not. This results in different outcomes if soil-bound heavy-metal flows are taken into account and therefore a higher value of D corresponds with a lower total metal content in the plough layer. Moreover, a steady-state situation will be reached if the metal input by compost or mineral fertilizer equals the output by soil-bound flows. According to the DB-approach, the steady-state Cd content will be reached sooner and it will stabilize at a lower level if the soil-bound Cd output flow becomes larger. The outcomes of the DSCB-approach give a different picture. It is clear that the DSCB-approach does not result in different soil contents if the output by soil-bound heavy-metal flows is taken into account by using different values for D. This results from using the correction factor. If the thickness of the layer that is added by applying SSO-compost exceeds the thickness of the layer that is taken off by soil flows, less soil will be leaving the plough layer than if soil flows were not accounted for. However, the resulting content is not influenced. In that case, it appears that the output by soil-bound flows does not count at all.

If the thickness of the layer that is added by applying SSO-compost is smaller than the thickness of the layer that is taken off by soil flows, soil from the subsoil will be added to the plough layer by ploughing. It depends on the composition of this soil how the calculation of the resulting soil content will be influenced by taking into account soil-bound flows. The composition of the deeper soil layer was assumed to be the same as the newly calculated composition of the plough layer itself, thus resulting in the same soil contents at different values for D.

In case I, the DSCB-calculations only result in lower total contents than the DB-calculations if D=0. Because there are no compost applications in case II, soil from beneath the plough layer will be added to the plough layer as the soil surface level decreases. This is the result of taking into account the changing soil composition (D=0,1,2) and dirt tare (D=1,2). In case II, the percentage organic matter and the reference value decrease to 0.8 % and 0.6 mg kg^{-1} (DW) respectively and the soil bulk density increases up to 1600 kg m^{-3}.

In case II, a comparable development of heavy-metal contents occurs for the DB- and DSCB-approaches if D=0. According to the DSCB-approach, a steady-state situation will be reached for organic matter if the rate of organic matter decomposition in the plough layer equals the rate of organic matter addition by the crop residues. However, there will not be a development towards a steady-state situation for the heavy-metal content if mineral fertilizers are applied.

This shows that with the DSCB-approach it is possible to distinguish the effect of the matrix of soil amendments on the resulting accumulation in the plough layer. If only mineral fertilizers are used, a quite different situation will occur compared with the use of SSO-compost on long time scales (Fig. 5.6).

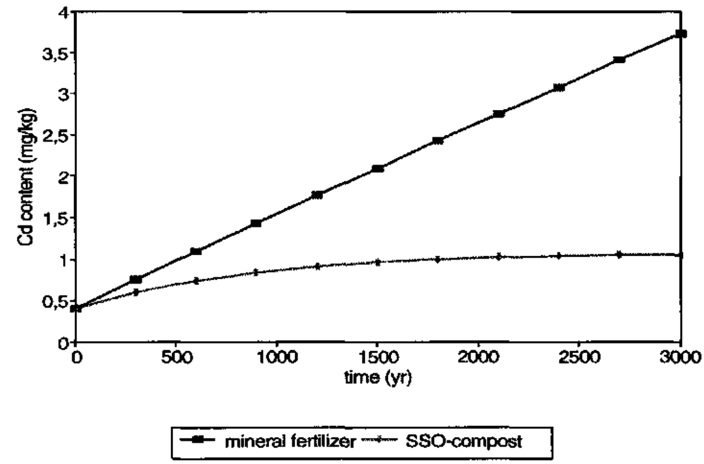


Figure 5.6. Development of the Cd content (mg kg^{-1} (DW)) in a loam soil according to the DSCB-approach in the case of Cd addition (0.44 mg m^{-2} yr^{-1}) by mineral fertilizer or SSO-compost only.

According to the DSCB-approach, the soil-bound output flows are of no relevance for the calculation of the resulting heavy-metal contents in the plough layer (Table 5.5). However, the composition of these flows still counts because the composition of dirt tare is very important in view of possibilities to dispose of the soil elsewhere.

Conclusion

Potential adverse effects of heavy-metal accumulation in the soil can only be prevented by adopting the approach of maintaining the metal balance in the receiving soil. This paper has given an overview of the main differences among the Static Balance, the Dynamic Balance and the Dynamic Soil Composition Balance (DSCB) approaches. The DSCB-approach for calculating heavy-metal accumulation is promising, because it takes into account the changes in soil composition. These changes, which are neglected in other balance approaches, were shown to be very important for an accurate and realistic balance calculation.
Taking into account the spatial boundaries and the properties of the system is very important for calculating the real accumulation of heavy metals in soil. Using a correction factor for plough layer thickness results in lower accumulation. Of course, the heavy metals did not 'disappear', but they are no longer part of the system here defined (*i.e.*, the plough layer) for calculating accumulation. Deeper soil layers will, according to these calculations, be enriched with heavy metals as well. This may result in a stratification of heavy metals, and more heavy metals

could become available for leaching and for uptake by biota because pH-values in the deeper soil layers are generally lower than in the plough layer. It is therefore wise to look further (*i.e.*, deeper) than the plough layer as well if heavy-metal accumulation is studied.

According to the DSCB-calculations, the heavy-metal and organic matter accumulation remain limited, because a steady-state situation is reached if compost applications continue 'for ever'. If the sustainability of applying SSO-compost is to be judged, it is important to determine whether accumulation will remain within safe limits in the long run.

Leaching and crop offtake (which depend on soil composition as well) were not incorporated in the illustrations. In a realistic scenario, the contribution of all relevant heavy-metal in- and output flows, like leaching, deposition, fertilizer applications, plant uptake and interception, erosion, and removal with dirt tare should be taken into account in an integrated model together with incorporation of the soil composition dynamics in the balance equation.

In the case of applying soil amendments with high soil and organic matter fractions, it is better to account for the composition of both the soil amendment and of the soil when calculating heavy-metal balances. The DSCB-approach is thus especially relevant if input consists of animal manure, other organic fertilizers or organic soil conditioners like SSO-compost. The practical implications of this new approach for setting limits with regard to heavy-metal input flows that are 'free' (deposition, mineral fertilizers) and input flows that are 'bound' to a soil matrix (organic amendments) should therefore be assessed. The distinction between output flows that are 'free' (*e.g.*, leaching and plant uptake) and that are 'bound' (*e.g.*, dirt tare and erosion) was shown to be very important for the different balance calculations as well. With the DSCB-approach these soil-bound heavy-metal flows can be accounted for correctly.

Acknowledgements

The mathematical and programming support of Dr. R. van Dijke and the information on organic matter dynamics given by Dr. B. Janssen (both: Department of Environmental Sciences), are highly appreciated.

Appendix: Method of calculating the correction factor *r*

Because of compost additions and soil composition dynamics, a correction factor (r) must be used to account for the growing topsoil and constant plough layer thickness.

At time t the plough layer thickness equals d. At time t^+, compost application takes place and the plough layer thickness is increased by d_c. Part of the original plough layer will become part of the new plough layer and part will be moved to a deeper soil layer. The resulting correction factor after the first compost application is $r = (d-d_c)/d$, because the 'compost fraction' of the new plough layer will equal d_c/d and the fraction of the original plough layer in the new plough layer equals $(d-d_c)/d$. However, at time $(t+1)^-$ the plough layer thickness has decreased because of the amount of organic matter that has been mineralized (d_v) during the first year. The correction factor for the second year (and all the

following years) must therefore be adjusted for this amount and becomes $r = (d-d_c)/(d-d_v)$.
If the removal of soil particles from processes like dirt tare offtake, wind erosion and runoff decreases the plough layer thickness, these processes must also be taken into account. If the plough layer thickness is decreased by dirt tare (d_t), wind erosion (d_w) and runoff (d_r), respectively, these fractions should be incorporated in *r*. The sum of these fractions is called d_o in the following equations.
If $d_c > d_v + d_o$, then $r = (d-d_c)/(d-d_v)$. This means that in this case the flows of heavy metals with dirt tare, erosion and runoff do not influence the correction factor at all; only the part of the plough layer that is moved deeper is decreased by these flows.
If $d_c < d_v + d_o$, then the soil from the subsoil will be ploughed into the new plough layer, because more soil is taken out from the plough layer than added to the plough layer. However, the composition of the soil that will be ploughed into the new plough layer is assumed to be the same as the composition of the plough layer itself. In this case the new value for *r* becomes:

$$r=(d^2-dd_c-d_vd_v-d_vd_o+d_cd_v)/d(d-d_v) \tag{5.8}$$

In all cases the amount (Q) of heavy metals, clay, sand, and organic matter at the beginning of every new year (or growing season) is:

$$Q_n=rQ_o+Q_e \tag{5.9}$$

Q is corrected with *r*, which is based on the new application at the very beginning of the year (t^+). After calculating the mass balance of all soil components, the heavy-metal contents are calculated at the end of every year (t^-) by the quotient of the total amount per unit area (content) and the plough layer weight (soil bulk density times d). The soil bulk density (ρ) is calculated according to an empirical formula based on Van Wijk & Beuving (1984), given by $\rho = 1/(0.6 + 3H)$.
The correction factor is used at the moment of compost application, which is taken to be at the beginning of the growing season of a certain crop. Hence, the subsequent calculation during that period is based on the new plough layer composition.
In the case of organic matter, the average amount of organic matter in a specific year is used as a basis for further calculations. Using the amount of organic matter at the moment of application would overestimate the fraction organic matter present, and using the amount at the end of the growing season would underestimate the fraction organic matter present. Because the fraction organic matter influences the value of the soil bulk density, this has to be taken into account. Taking the average amount for a specific year avoids the extremes and gives a realistic basis for further calculations.
In the model calculations, the yearly heavy-metal additions are all added up. This results in a constant and average heavy-metal input in time. This is reasonable for long-term diffuse source soil contamination. That is also why an average fraction organic matter was used every year instead of a fraction calculated by *e.g.*, interpolation. Although interpolation enables calculations on a more detailed time-scale, it would also require more detailed information about decomposition patterns during a year.

Symbols:

d: plough layer thickness (constant at 0.25 m)
d_c: thickness of the layer of yearly applied organic material (m)
d_v: thickness of layer disappearing because of organic matter decomposition (m)
d_t: thickness of layer of soil lost through dirt tare (m)
d_e: thickness of layer of soil lost through wind erosion (m)
d_r: thickness of layer of soil lost through surface runoff (water erosion; m)
d_o: thickness of layer of soil lost through dirt tare, wind and water erosion (m)
t: time (yr)
t^+: the very beginning of the year (right after compost application)
t^-: the end of the year (just before a new compost application)
r: plough layer thickness correction factor (-)
Q_n: new amount of organic matter, clay, sand, and heavy metals (g m^{-2})
Q_0: amount of soil constituents in the year before the year of calculation (g m^{-2})
Q_e: added amount of soil constituents (g m^{-2})
ρ: dry soil bulk density (kg m^{-3})

CHAPTER 6

HEAVY-METAL BALANCES OF AGRO-ECOSYSTEMS IN THE NETHERLANDS

Abstract

In this chapter, heavy-metal flows of arable, dairy and mixed farming systems in the Netherlands are studied. Farm-gate and field-scale balances are calculated. On the field-scale, static and dynamic balances are distinguished. By determining the characteristic metal flows, it becomes possible to differentiate between farming systems and to select the most viable options for sustainable heavy-metal management. The crop rotation and the choice of fertilizers clearly influence the heavy-metal balance of arable farming systems. In dairy farming systems, the role of feed management is very important, but the effects on the heavy-metal balance are not always straightforward. Mixed farming systems compare favorably with specialized (arable or dairy) farming systems with regard to heavy-metal accumulation. Due to the internal cycling of feedstuff and manure, less inputs are required and thus the import of heavy-metal containing raw materials and products is minimized. Some uncertainties related to the calculation of heavy-metal balances are discussed.

Introduction

Accumulation of heavy metals in agricultural soil may cause problems if certain levels are exceeded. If soil is to permanently fulfil its functions in agricultural production, in environmental processes, and as a habitat of numerous organisms, heavy-metal accumulation has to be restricted. To this end, heavy-metal flows in agro-ecosystems have to be analyzed to identify the most important sources and processes that lead to accumulation. Based on such an analysis, preventive measures may be defined.

The balance approach has proven to be useful in soil fertility studies to demonstrate depletion of nutrients from soils (*e.g.*, Frissel, 1978; Smaling, 1993). This approach can also be used in soil pollution research to demonstrate accumulation of heavy metals in agricultural soils (Van Driel & Smilde, 1990). Heavy-metal balances thus serve to identify both management options and emissions from the soil to other environmental compartments.

In this chapter, we analyse Cd, Cu, Pb, and Zn flows and their balances at field and farm level for arable, dairy and mixed farming systems in the Netherlands. Quantifying the characteristic flows from literature data and measurements at experimental farms allows comparison of different systems and identification of the most viable options for sustainable heavy-metal management.

Modeling heavy-metal flows on different spatial scales

The spatial scale of analysis influences the calculation of heavy-metal balances. Analyses at national level cannot pay attention to relevant processes on smaller scales, because site-specific aspects are averaged out. It is therefore necessary to study heavy-metal balances on farm and field scale as well to get insight in the extent of accumulation in different agro-ecosystems (Chapter 3).

Farm-gate balance

If the agro-ecosystem's borders are drawn at the farm-gate, an analysis at farm level can be carried out. The input and output flows vary strongly among farming systems and the farm-gate balance shows the characteristic flows and processes of a farm as a whole. The farm-gate balance is useful, since management measures take place at farm level.

Field-scale balance

An analysis on farm scale does not distinguish among the soil, animal and plant compartments. The input and output flows between these compartments (*i.e.*, internal flows) vary largely among farming systems. The field-scale balance shows the balance sheets for the soil compartment or the plough layer of individual fields. In arable farming systems, the balance on farm and field scale is almost identical. If internal flows play an important role, as in dairy and mixed farming systems, the

farm-gate balance differs from the field-scale balance.
A balance equation for the plough layer relates the rates of change in heavy-metal content, input and output. A detailed description of the static and dynamic balance approaches is provided in Chapter 4 (Eqs. 4.1 - 4.11).

Arable farming system

Arable farming systems are characterized by their crop rotation. In such systems, the most important inputs are mineral (N, P, K) fertilizers, animal manure, organic amendments (sewage sludge and compost), and atmospheric deposition. The output consists of produce (crops) and leaching out of the plough layer. Since the internal cycle is represented by transfer of crop residues only, it is quite small (Figure 6.1).

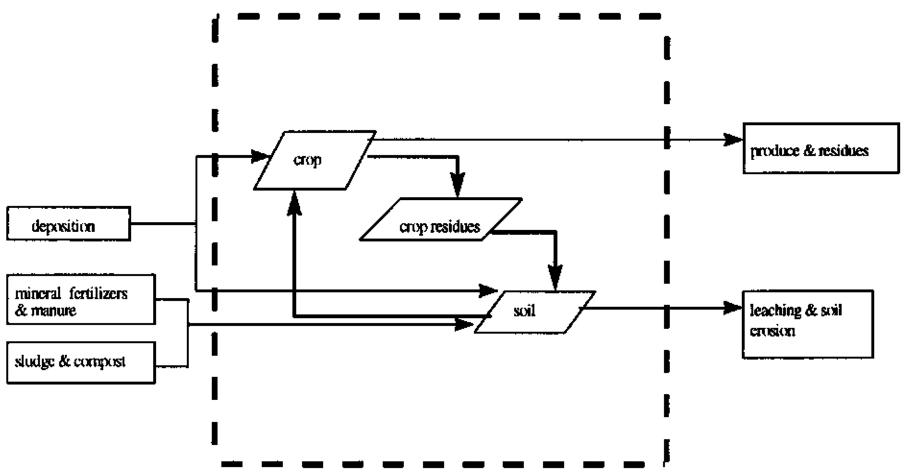


Figure 6.1. Arable farming system; input, internal (heavy solid arrows), and output flows.

Three arable farming systems as practised at Nagele experimental farm (in the Northeast polder; 52°39′ N, 5°44′ E) were chosen for this study *i.e.*, conventional (CAFS: 22.7 ha), integrated (IAFS: 17 ha), and ecological (EAFS: 22.2 ha). The 4-year crop rotation of the conventional system consists of ware and seed potato, sugar beet, chicory and onion, winter wheat and spring barley. This system comprises two parts, one with mineral fertilizers only (CAFS-MF: 14 ha) and one with both mineral and organic fertilizers (CAFS-OF: 8.7 ha). The crop rotation in the integrated system is similar to that in the conventional system (carrot instead of chicory). The 6-year crop rotation of the ecological system consists of seed potato, spring wheat, celery and onion, spring barley, carrot, and oats (Vereijken, 1992).

Heavy-metal balance sheets for the three systems were calculated. Soil samples were taken from the plough layer (top 30 cm) of each individual field (30 samples in total) and analysed for Cd, Cu, Pb, and Zn. General soil characteristics and average heavy-metal contents are given in Table 6.1. Detailed information on soil, fertilizer, and plant analyses is given in Hatziotis (1995) for Cd and Zn and in Van Kuik (1995) for Cu and Pb.

Table 6.1. General characteristics and heavy-metal contents of the Nagele soil.

pH-KCl:	7.4
Organic matter content (mass %):	2.6
Clay content (mass %):	24
$CaCO_3$ content (mass %):	10
ρ (kg m^{-3}):	1400
P_w -number:	25
K-number:	17
Cd content (mg kg^{-1} DW):	0.5 (0.48-0.52)
Cu content (mg kg^{-1} DW):	23 (19-27)
Pb content (mg kg^{-1} DW):	35 (33-38)
Zn content (mg kg^{-1} DW):	100 (99-107)

DW: dry weight

Inputs

At Nagele, the most important sources are atmospheric deposition and fertilizer application. Irrigation water samples from a nearby ditch did not show detectable levels of heavy metals. Inputs via atmospheric deposition were based on measurements at Biddinghuizen near Nagele (Aben *et al.*, 1992). During the growing season 1993-1994, various fertilizers were used: in CAFS-MF mineral fertilizer only, in EAFS organic fertilizers (solid goat and cattle manure) only, and in IAFS and CAFS-OF a combination of organic and mineral fertilizers. Phosphate requirements were met with liquid poultry manure in IAFS and CAFS-OF and with triple superphosphate (TSP) in CAFS-MF. Nitrogen and potassium requirements were met with ammonium nitrate limestone (CAN) and muriate of potash (K-60), respectively. Fertilizer applications and heavy-metal contents in these fertilizers are shown in Table 6.2 and Table 6.3, respectively.

Table 6.2. Manure and fertilizer inputs (kg dry weight) in the growing season 1993/1994 and surface area (ha) for the farming systems at Nagele experimental farm.

	Ecological	Integrated	Conventional	
			organic fert.	mineral fert.
Surface area	22.2	17	8.7	14
Poultry manure	0	19695	11263	0
Goat manure	45859	0	0	0
Cattle manure	16352	0	0	0
CAN	0	4250	1782	5367
K-60	0	4887	2322	5211
TSP	0	0	0	2025

CAN: ammonium nitrate limesone; K-60: muriate of potash; TSP: tripel super phosphate

Table 6.3. Heavy-metal contents in manure and fertilizers (mg kg^{-1} dry weight) used at Nagele experimental farm.

	Cd	Cd (mg kg^{-1} P_2O_5)	Cu	Pb	Zn
Poultry manure	0.42	7.7	72.7	4.9	647
Goat manure	0.38	30.6	45.9	11.9	157
Cattle manure	0.37	20.7	33.2	31.9	167
CAN	0	-	0.45	0.4	1.78
K-60	0	-	0.48	1.1	1.38
TSP	31.4	68.4	43.9	3.9	593

CAN: ammonium nitrate limesone; K-60: muriate of potash; TSP: tripel super phosphate

Crop removal

Total metal removal in crops is calculated from yield (defined as dry weight at economic maturity stage) removed from the fields and crop metal contents. Green materials recycled within the farm (such as grass, clover, lucerne, leaves of sugar beet, and leaves of celeriac) are not included in the calculation of total output. Straw was taken off the field and sold. The area-weighted mean values for crop removal of the 4 farming systems are shown in Table 6.4. Output in produce is lowest in EAFS since crop yields are lowest. Moreover, sugar beet (with a high offtake of Cu, Zn, Cd) is not produced and part of the area is used as so-called ecological infrastructure on which grass/clover/lucerne and hedgerows are grown.

Table 6.4. Area-weighted mean heavy-metal offtake by crops (g ha^{-1} yr^{-1}) in four arable farming systems (and average numbers for the conventional systems) at the Nagele farm.

	Cd	Cu	Pb	Zn
Ecological	0.6	33.3	1.24	138
Integrated	0.94	48.7	1.58	204
Conventional (organic fert.)	0.78	58.3	2.62	190
Conventional (mineral fert.)	0.82	50.5	2.2	187
Conventional (average)	0.81	53.5	2.35	188

Leaching

Metal solubility is expected to be low in this calcareous soil. As Cd, Cu, Pb and Zn co-exist in the soil solution, we have determined competitive adsorption isotherms for the mixture of Cd, Cu, Pb and Zn at soil pH in order to determine the solute concentrations. The concentration ranges in the mixture correspond to those resulting from deposition and fertilizers. The competitive cations Ca, Na, and K were added in the ratio 3:1:1.

Lead was not present in detectable concentrations (< 16 $\mu g\ l^{-1}$) in the equilibrium solution. Hence, no adsorption isotherm could be constructed. For Cd, Cu and Zn, a Freundlich type relationship between concentration in solution (c) and adsorbed amount (q) could be fitted (Table 6.5). The initial solution concentrations calculated by substituting the q_i values (Table 6.5) in the adsorption models for Cd, Cu and Zn equal 0.02, 2.7, and 0.2 (mg m^{-3}), respectively. Multiplying these concentrations with the precipitation surplus of 0.3 m yr^{-1}, results in leaching rates of 0.06, 8.1, and 0.6 g ha^{-1} yr^{-1} for Cd, Cu and Zn, respectively.

Table 6.5. Adsorption models for Cd, Cu, and Zn in the Nagele soil expressing the relationship between concentration in solution (c: mg m^{-3}) and the adsorbed amount (q: mg kg^{-1}). The initially adsorbed amount is given by the value of q_i.

	adsorption model	r^2	q_i
Cd:	$c = 0.19q^{1.47}$	0.99	0.24
Cu:	$c = 0.026q^{1.46}$	0.89	23.8
Zn:	$c = 3.54\ 10^{-6}q^{2.79}$	0.99	51.7

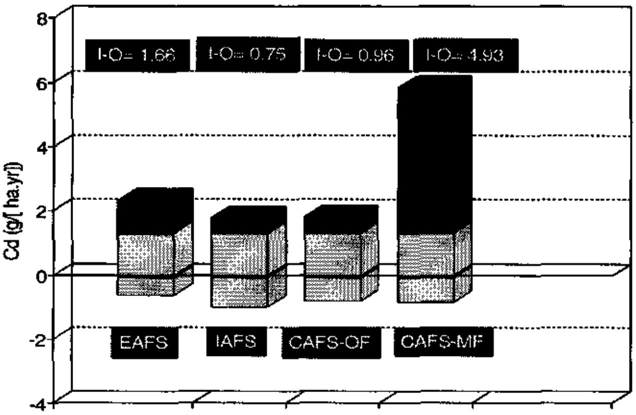
Balances

The static balances of Cd, Cu, Pb and Zn in the farming systems are presented in Figures 6.2a-6.2d, respectively (leaching and crop offtake: negative y-axis; fertilizers and deposition: positive y-axis).

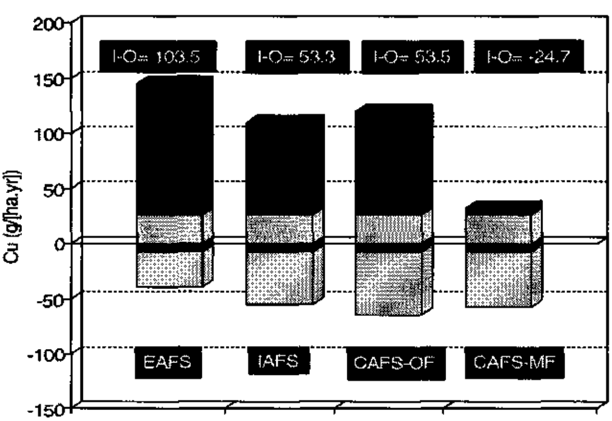
As an illustration of long-term simulation, the dynamic balance approach was applied to Cd and Cu, which represent extreme cases in the conventional arable farming system (CAFS-'average'). Soil bulk density and plough layer thickness may not be constant in time due to changes in organic matter content and input or output of soil particles by processes like erosion. This is recognized by the so-called dynamic soil composition balance approach (DSCB), which takes into account changes in soil composition while calculating the dynamic balance (Chapter 5). Because these changes in soil composition are not known, they are not regarded in this analysis.

The values for the input rates (A: Tables 6.2, 6.3 and Figures 6.2a,b), removal rates by harvest (U: with area-weighted mean values of the individual B values given in Table 6.6), and leaching rates (L: with solute concentration based on the adsorption models in Table 6.5) were substituted in the dynamic balance equations (Eqs. 4.2-4.11).

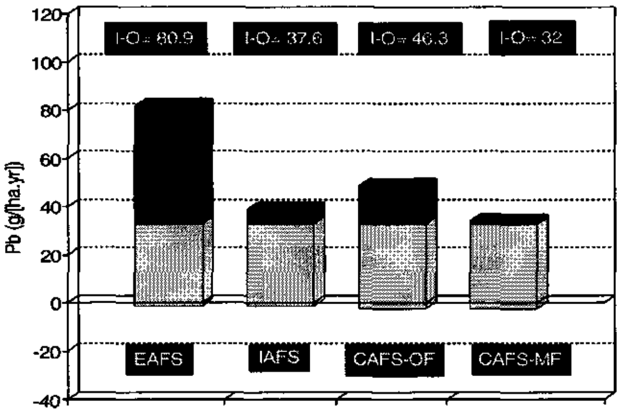
(a)


I-O= 1.66
I-O= 0.75
I-O= 0.96
I-O= 4.93
Cd (g/[ha.yr])
8
6
4
2
0
-2
-4
EAFS
IAFS
CAFS-OF
CAFS-MF

(b)


I-O= 103.5
I-O= 53.3
I-O= 53.5
I-O= -24.7
Cu (g/[ha.yr])
200
150
100
50
0
-50
-100
-150
EAFS
IAFS
CAFS-OF
CAFS-MF

(c)



(d)

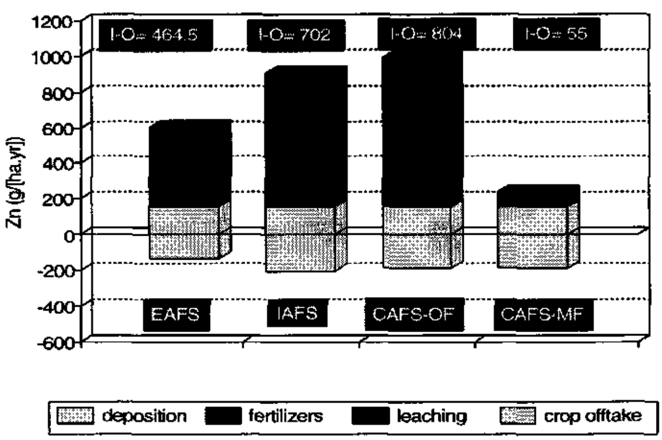


Figure 6.2. Annual Cd (a), Cu (b), Pb (c), and Zn (d) input (I) and output (O) flows for ecological (EAFS), integrated (IAFS), and conventional (mineral fertilizers only: MF, mineral and organic fertilizers: OF) arable farming systems at Nagele experimental farm.

Table 6.6. Cd and Cu uptake rate constants (B: 10^{-4} yr^{-1}) for different arable farming systems at Nagele experimental farm (area-weighted mean values).

	Ecological	Integrated	Conventional		
			organic fert.	mineral fert.	'average'
Cd	5.92	10.43	9.07	7.99	8.4
Cu	3.39	5.31	5.78	5.19	5.42

The development of soil content, leaching and uptake in the conventional system (total) is shown in Figures 6.3 (Cd) and 6.4 (Cu). Soil Cd content will exceed the Dutch reference value (defined as [0.4 + 0.007{C + 3H}] with mass % clay (C) and mass % organic matter (H), *i.e.*, 0.6 mg kg^{-1} for this soil) and develop towards a steady-state value of ca. 1.7 mg kg^{-1} (Figure 6.3).

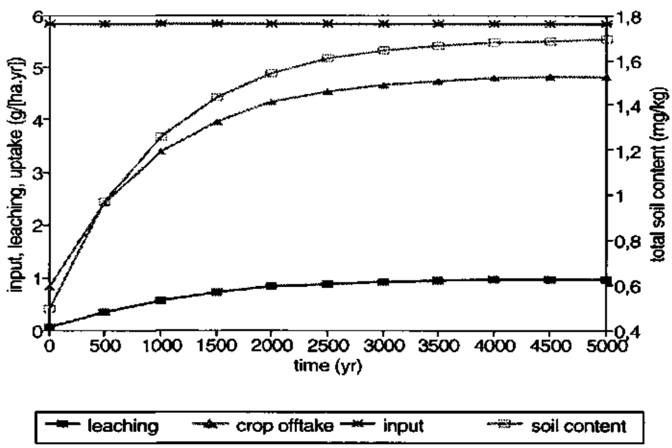


Figure 6.3. Development of Cd input and soil content, leaching and uptake rates in the conventional arable farming system.

The high (average) offtake rate will result in quality standards of some crops being exceeded (Chapter 9). Figure 6.4 shows that the Cu soil content decreases to 14 mg kg^{-1} at steady state, with the associated reduction in leaching and crop offtake.

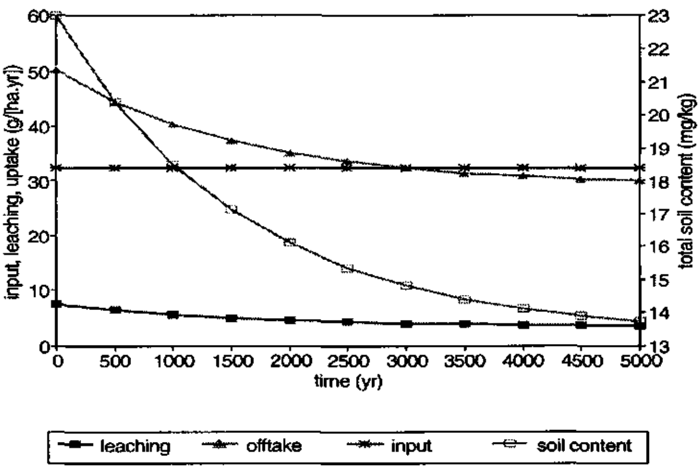


Figure 6.4. Development of Cu input and soil content, leaching and uptake rates in the conventional arable farming system.

These dynamic balance calculations illustrate that it is possible to compare and judge the long-term behavior of different heavy metals. Atmospheric deposition, crop rotation and selection of fertilizers directly influence both the annual balance and the long-term development of heavy-metal concentrations in soil, groundwater and crops.

Dairy farming system

Dairy farming is the most important sector of Dutch agriculture. It occupies ca. 65% of the cultivated area and provides the main income to 35% of the Dutch farmers. A dairy farm is characterized by the combination of plant and animal production (Figure 6.5). The most important compartments in dairy farming are soil, roughage (grass and possibly maize), manure and livestock. In general, heavy-metal flows in dairy farming systems are smaller than in arable farming systems. However, due to the internal cycles, the balance may be more difficult to influence by farm management.

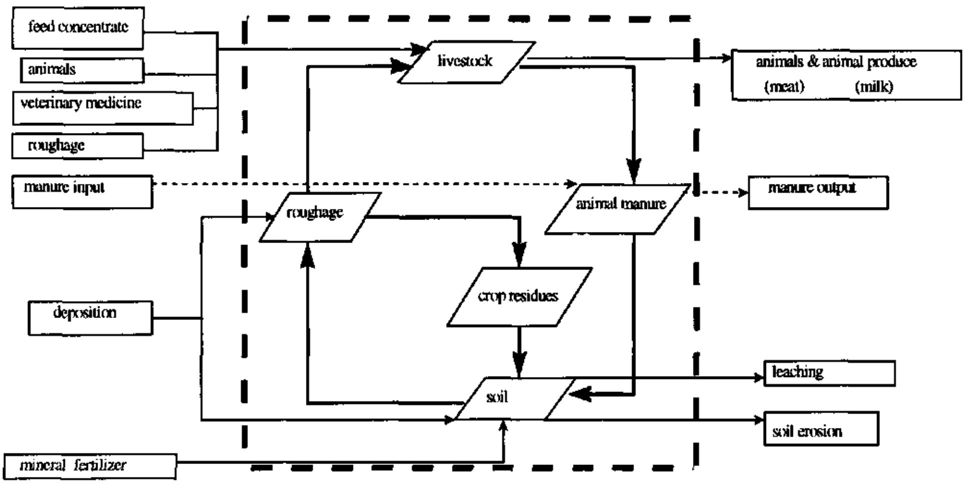


Figure 6.5. Dairy farming system; input, internal (heavy solid arrows), and output flows.

Manure is not always imported since on-farm manure production may be (more than) sufficient. In Figure 6.5, possible inputs through biocides, detergents for disinfection and cleaning, drinking, irrigation and cleaning water, artificial milk, seeds and others are neglected. For example, the heavy-metal balance is influenced by the number of animals and forage production, which influence the amount of inputs required. In the past, milk production systems were characterized by careful use of animal manure as part of the integration of arable and dairy farming. These systems have been strongly intensified through increased inputs of mineral N-fertilizers and purchased feeds which has led to a serious imbalance between inputs of nutrients and outputs in milk and meat. On Dutch dairy farms, average annual milk production is about 11500 kg ha^{-1} and output represents on average 14% of the input for N, 32% for P, and 17% for K (Aarts *et al.*, 1992). Fertilizer application rates vary widely within the same type of farming system. Poppe *et al.* (1994) found a mean application rate of 250 kg N ha^{-1} with a range of ca. 100-360. Higher N-fertilizer applications result in slightly higher heavy-metal inputs. However, they may also lead to increased forage production and consequently lower inputs of purchased feed (roughage and concentrates) and associated heavy-metals.
Van Hooft (1995) established the risks for public health due to uptake of heavy

metals by cows during grazing. The transfer coefficients from soil to animals depend on absorption, internal distribution, and retention of the elements in the animal's body. Cadmium and Pb end up mainly in liver and kidney and Cu in the liver. Muscular tissue and milk are hardly contaminated with heavy metals. Animal intake of grass (including adhering soil), other roughages, and feed concentrates were identified as the most significant sources of heavy-metals in cows. Inhalation, dermal uptake, and water consumption were not considered to be significant pathways of exposure. Most heavy metals ingested are excreted and only ca. 5% is retained in the body (Van Hooft, 1995).

Vreman & Vos (1987) carried out an extensive survey of heavy-metal contents in raw materials used for feed production of plant, animal and mineral origin. They concluded that contents in raw materials and in concentrates also depend on additions and contamination during production, transport and storage of the feed. They showed that although Cd contents in raw materials generally were below the detection limit, in the concentrates they were higher due to contamination during processing.

Metal contents in animal manure can be estimated in various ways. Total intake with feed can be calculated by measurement of feed consumption and contents. The contents in manure may then be derived from the fraction retained in the animal. Alternatively, manure samples may be analyzed directly. The first approach was followed by Van der Veen *et al.* (1993) by calculating mineral balance sheets for monitored farms. They assumed that applications of animal manure and mineral fertilizer determine crop yield, which in turn determines roughage availability. Feed requirements were based on milk production per animal, and the feed balances yield the buying and selling of roughage and the manure production. IKC (1997) used both approaches in a complementary way to calculate heavy-metal balances for dairy farming systems with varying soil type (sand, clay, peat), livestock density (1.5, 2.25, 3 dairy cows per hectare), and growing of silage maize (clay and peat: 0% of farm area; sand: 20 or 30% of farm area). The inputs consisted of roughage, concentrates and mineral fertilizers. The outputs consisted of meat, milk, roughage, and animal manure. All systems show a Cd surplus which is largely determined by fertilizer use. Fattening pig manure systems show the highest Cu surplus, since Cu is added to feed concentrates (albeit in lower contents than in the past). Fattening pig manure also causes the highest Zn surplus in the fertilization scenarios, followed by systems with high livestock concentrations. The latter have high Zn inputs due to imported silage maize (roughage) and formula feed (concentrate). These findings were confirmed by Blaauw & Kuypers (1994), who found that for the field-scale balance of a hypothetical specialized dairy farming system, the most important inputs were mineral fertilizers (Cd, Pb), concentrates (Cd, Cu, Zn), deposition (Pb, Cu, Zn), and roughage (Zn).

Mixed farming system

The mixed farming system (Figure 6.6) is very similar to the dairy farming system except that there may be output of roughage (grass and maize) and arable crops.

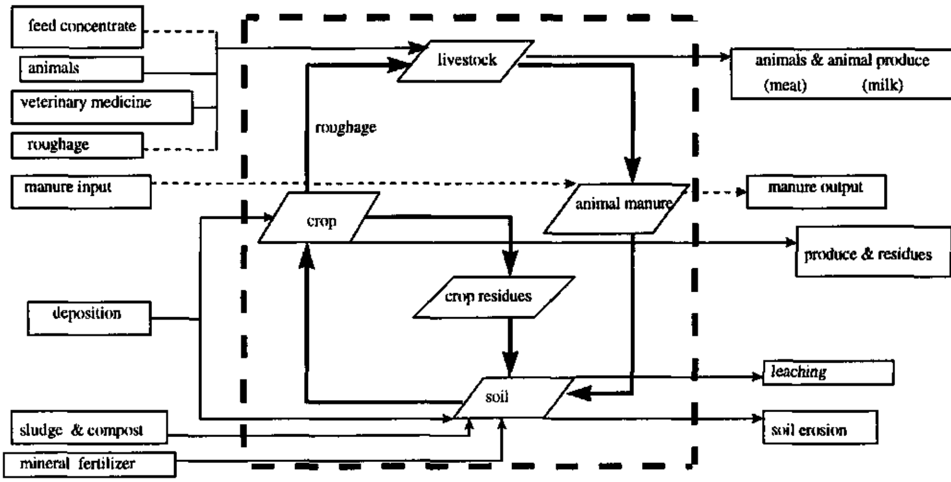


Figure 6.6. Mixed farming system; input, internal (heavy solid arrows), and output flows.

External inputs as mineral fertilizers, concentrates and biocides were not used in large quantities until the second half of this century, as production was based on locally available resources from recycling of minerals in manure and other 'waste'. Since the 50's, technological innovations, cheap raw materials, higher wages, and favorable terms of trade for agricultural products have resulted in increases in production, savings on labor and further specialisation and intensification. The mixed farming systems, which were especially common on sandy soils, disappeared, and currently 90% of all dairy farming is concentrated on specialized farms (Aarts & Van Gorp, 1989).
Lantinga & Rabbinge (1996) plead for 'a renaissance' of mixed farming systems to reduce the use of external inputs and increase the efficiency of external inputs by recycling of plant and animal products. Moreover, labor may be better utilized and income risks spread. Another motive for re-integration is the lack of perspectives for current arable farming systems in the Netherlands (Anonymous, 1992a) and

therefore more viable farming types could be developed by mixing arable farming with either intensive husbandry systems or dairy farming systems (within a single farm or on a regional scale), or production of concentrate substitutes on dairy farms. By mixing land-bound farming systems (*i.e.*, arable and dairy farming), substance cycles could be closed by the exchange of forage crops with manure, and crop rotations could be widened which would result in less diseases and the potential for growing more profitable crops. Model studies indicate that this combination may improve both economic and ecological results (De Koeijer *et al.*, 1995). On experimental farm 'The Minderhoudhoeve' (near Swifterbant in the Flevopolder: 52° 33′ N, 5° 40′ E), two different mixed farming systems of this type are being developed: an integrated farm (135 ha) and an ecological farm (90 ha). Further details on the research plan of both mixed farms are provided in Lantinga & Van Laar (1997). We calculated heavy-metal balances at the farm and field level based on the input, output, and internal flows as described in this research plan. Additional information on crop yields was found in Aarts (1991) and Roeterdink & Haaksma (1993). Literature data were used on heavy metals in atmospheric deposition (Aben *et al.*, 1992), leachate (Breimer & Smilde, 1986; Ferdinandus *et al.*, 1989 Van Erp & Van Lune 1991; Boumans & Wessels, 1993; Van Duivenbooden *et al.*, 1995), mineral fertilizers (Van Erp & Meeuwissen, 1994; De Boo, 1995; Driessen & Roos, 1996), animal manure (Driessen & Roos, 1996), source-separated organics (SSO) compost (Van Erp & Evers, NMI, pers. comm.), concentrates (Anonymous, 1994), meat (De Boo, 1995), milk (Anonymous, 1985; Anonymous, 1990), arable crops (Van Erp & Meeuwissen, 1994, De Boo, 1995), grass, and feed crops (Anonymous, 1985; Van Erp & Meeuwissen, 1994; De Boo, 1995). Runoff, offtake with soil adhering to crops, and soil ingestion by cows were not accounted for. Opschoor (1996) gives a detailed description of the calculations. Table 6.7 shows the farm-gate balance of the integrated mixed farming system.

Table 6.7. Farm-gate balance sheets of heavy metals (g ha^{-1} yr^{-1}) of the integrated mixed farming system at the Minderhoudhoeve.

	Cd	Cu	Pb	Zn
Input (I):				
Mineral fertilizers	1.37	1.2	1.5	16.2
Feed concentrates	0.05	16.5	0.5	52.8
Deposition	1.3	25.6	33.1	156.0
Total	2.72	43.3	35.1	225.0
Output (O):				
Crops	0.66	25.7	3.9	101.1
Milk	0.007	0.2	0.03	21.6
Meat/animal	0.0007	0.4	0.002	6.4
Leaching	1.6	43.1	14.8	63.3
Total	2.3	69.4	18.7	192.4
I-O	0.42	-26.1	16.4	32.6

The internal flows in the integrated mixed farming system consist of cow manure and roughage (grass, clover, fodder beets, silage maize). These flows are not part of the farm-gate balance, but they are important for the field-scale balance (Table 6.8).

Table 6.8. Total (grassland and arable land combined) field-scale balance sheet (g ha^{-1} yr^{-1}) of the integrated mixed farming system at the Minderhoudhoeve.

	Cd	Cu	Pb	Zn
Input (I):				
Fertilizers/manure	2.2	132.9	54.2	543.3
Deposition	1.3	25.6	33.1	156.0
Total	3.5	158.5	87.3	699.3
Output (O):				
Arable crops	0.66	25.7	3.9	101.1
Grass & forage crops	1.1	62.8	12	665.4
Leaching	1.6	43.1	14.8	63.3
Total	3.4	131.6	30.7	829.8
I-O	0.1	26.9	56.6	-131

On mixed farms, part of the land is grassland and part is used for growing arable and forage crops. The integrated farm comprises 41 ha grassland and 94 ha arable land. We derived separate field-scale balances for grassland and arable land. Grassland is amended with N-fertilizer and manure (52 ton ha^{-1}). The grass/clover mixture receives 18 ton manure per ha. Table 6.9 shows the heavy-metal balances for the grassland.

Table 6.9. Field-scale balance sheet (g ha^{-1} yr^{-1}) of grassland of the integrated mixed farming system at the Minderhoudhoeve.

	Cd	Cu	Pb	Zn
Input (I):				
Fertilizers/manure	2.4	219.1	89.6	876
Deposition	1.3	25.6	33.1	156
Total	3.7	244.7	122.7	1032
Output (O):				
Grass offtake	1.4	161.6	27.4	1378
Leaching	1.6	43.1	14.8	63.3
Total	3.0	204.7	42.2	1441.3
I-O	0.7	40.0	80.5	-409

Arable land is amended with about the same amount of N-fertilizer as grassland and with P-fertilizer and manure.

Table 6.10 shows the heavy-metal balances for the arable land.

Table 6.10. Field-scale balance sheet (g ha^{-1} yr^{-1}) of arable land of the integrated mixed farming system at the Minderhoudhoeve.

	Cd	Cu	Pb	Zn
Input (I):				
Fertilizers/manure	2.1	95.4	38.7	387.5
Deposition	1.3	25.6	33.1	156.0
Total	3.4	121.0	71.8	543.5
Output (O):				
Feed crops	0.95	19.7	5.2	354.5
Arable crops	0.65	25.7	3.9	101.1
Leaching	1.6	43.1	14.8	63.3
Total	3.2	88.5	23.9	518.9
I-O	0.2	32.5	47.9	24.6

Heavy-metal balances may be calculated for the livestock compartment as well (Table 6.11).

Table 6.11. Heavy-metal balance sheet (g) of the livestock compartment in the integrated mixed farming system at the Minderhoudhoeve.

	Cd	Cu	Pb	Zn
Input (I):				
Concentrates	7	2226	74	7122
Roughage	146	8476	1618	89826
Total	153	10702	1692	96948
Output (O):				
Milk	1	27	4	2914
Animal/meat	0.1	49	0.2	863
Manure	107	17790	7116	71160
Total	108	17866	7120	74937
I-O (g)	45	-7164	-5428	22011
I-O (g cow^{-1})	0.24	-37.7	-28.6	116
I-O (g ha^{-1})	0.33	-53.1	-40.2	163

In the ecological mixed farming system, SSO-compost provides half the required P-input. The farm-gate balance of the ecological mixed farming system is shown in Table 6.12.

Almost all arable and forage crops are used for animal feed, hence crop offtake is restricted to 6 ha root crops. The field-scale balance of the ecological mixed farming system is shown in Table 6.13. Internal flows consist of cow manure and practically all crops.

Table 6.12. Farm-gate balance sheet (g ha^{-1} yr^{-1}) of the ecological mixed farming system at the Minderhoudhoeve.

	Cd	Cu	Pb	Zn
Input (I):				
Mineral fertilizers	0.03	2.7	3.0	8.9
SSO-compost	1.7	83	198	489
Concentrates	-	-	-	-
Deposition	1.3	25.6	33.1	156.0
Total	3.03	111.3	234.1	653.9
Output (O):				
Crop produce	0.36	17.6	1.4	253.8
Milk	-	0.18	0.02	19.3
Meat/animals	-	0.36	-	6.4
Leaching	1.6	43.1	14.8	63.3
Total	2.0	61.2	16.2	342.8
I-O	1.0	50.1	218	311

Table 6.13. Total (grass and arable land combined) field-scale balance sheet (g ha^{-1} yr^{-1}) of the ecological mixed farming system at the Minderhoudhoeve.

	Cd	Cu	Pb	Zn
Input (I):				
Mineral fertilizers	0.03	2.7	3.0	8.9
SSO-compost	1.7	83	198	489
Animal manure	0.6	100.0	40.0	400.0
Deposition	1.3	25.6	33.1	156.0
Total	3.63	211.3	274.1	1053.9
Output (O):				
Crop offtake (all)	1.5	100.7	13.6	999.1
Leaching	1.6	43.1	14.8	63.3
Total	3.1	143.8	28.4	1062.4
I-O	0.53	67.5	246	-8.5

Comparisons

Arable farming

Regarding to the total Cd input at Nagele experimental farm, only for CAFS-MF is addition through atmospheric deposition lower than addition through fertilization (Figure 6.2a). The Cd balance of CAFS-MF shows a much larger accumulation than for CAFS-OF due to the Cd inputs with triple superphosphate applications. Copper and Zn inputs are highest when animal manures are applied and the contribution of atmospheric deposition only exceeds that of fertilizer in CAFS-MF (Figures 6.2b and 6.2d).

Cultivation of crops with a high Cd offtake (carrots, sugar beets, ware potatoes and onions) also influences the Cd balance. EAFS has a higher Cd input/output ratio

than IAFS and CAFS-OF because a larger percentage of the total area is grain crops with limited Cd offtake. Also, inputs via manure are higher in EAFS, partly due to large applications to raise the P status of the soil.
Clearly, crop rotation and the selection of fertilizers directly influence the heavy-metal balance of arable farming systems. Optimization models may be used to formulate fertilizer plans that meet constraints on heavy-metal input via fertilizers, but also on other agricultural, legislative and economic constraints, based on farm-specific information. Velthof *et al.* (1996), using such an optimization model for arable farming, indicated that it is not possible to formulate fertilizer plans in which input and output balance for Cd, Cu and Zn concurrently. Minimizing Cd input increases Cu and Zn inputs and minimizing Cu and Zn inputs increases Cd input due to substitution between animal manure and mineral fertilizer. This is also shown in the Nagele study. The integrated system compares favorably with the conventional (MF) system with respect to Cd, but the reverse holds for Cu, Pb and Zn, mainly due to different fertilizers used in these systems.
Based on recent measurements of heavy-metal contents in different kinds of fertilizers, manures and composts, IKC (1997) calculated the heavy-metal balances for arable farming on a clay soil (50% grains, 25% potatoes, 25% sugar beet) with different fertilizer plans (cattle, pig and broiler manure, compost, mineral fertilizers) representative of Dutch arable farming. Comparing the results of Nagele experimental farm with some scenarios by IKC (1997) shows that EAFS and CAFS-MF have a comparable Cd surplus for comparable fertilizer plans. Cadmium depletion only occurs in IAFS and CAFS-OF (no mineral P-fertilizer and less manure applied). Depletion of Cu and Zn is comparable for CAFS-MF and the fertilizer plans with mineral fertilizers only. However, Cu and Zn surplusses in the animal manure scenarios are much higher than those of Nagele farm due to the other types of fertilizers used (pig manure and compost) and the higher amounts applied. The Pb balances are similar in both studies.

Dairy farming

In dairy farming systems, the role of feed management is very important, but the effects on the heavy-metal balance may not always be straightforward.
The proportion of forage produced on-farm should be maximized to restrict the need for purchased feeds, with its external inputs of minerals and heavy metals. However, the quantity and quality of roughage produced is not sufficient to satisfy the total feed demand, and therefore concentrates are imported. Growing concentrate substitutes on-farm may result in less grassland available for roughage production, which results in more intensive grassland use (*i.e.*, higher N-levels) to secure a sufficient roughage supply. Hence, growing concentrate substitutes does not necessarily result in lower heavy-metal inputs. If the land is suitable for growing both grass and concentrate substitutes, land allocation to the different crops may be optimized, taking into account both the desired quantities and qualities of forages, and the possibility to apply animal manure.

Mixed farming

Comparing Tables 6.7 and 6.12, shows that input with SSO-compost in the ecological system far exceeds the combined input with fertilizers and concentrates in the integrated system.

Tables 6.9 and 6.10 show for Cu, Pb and Zn in the integrated system that both the input in fertilizers and the output in crop products is (much) larger on grassland than on arable land. The balances show a larger Cd, Cu and Pb surplus for grassland than for arable land. On arable land, Zn accumulates and on grassland Zn depletion occurs.

It should be noted that for both the ecological farm and the integrated farm a discrepancy exists between the farm-gate balance and the total field-scale balance (Tables 6.7 and 6.8; Tables 6.12 and 6.13). Since the heavy metals do not degrade or volatilize, the difference must be in the livestock compartment (Table 6.11). This is discussed in the next section on uncertainties.

Uncertainties

For effective heavy-metal management and strategic decision making, insight is needed into the relationships and uncertainties in the balance calculations. In the case of deterministic variables, there is no uncertainty associated with a certain value. Calculations according to the static and dynamic balances were carried out deterministically, while in reality the values of G, A, L, and U vary and should thus be considered uncertain. The following discussion of the balance in the livestock compartment, leaching and SSO-compost illustrate some uncertainties involved.

Livestock compartment balance

The heavy-metal balance of the livestock compartment in the integrated mixed farming system (Table 6.11) shows inconsistencies. According to the calculations, Cd and Zn accumulate in the cows in relatively large amounts, while Cu and Pb seem to be 'produced' by the cows. This discrepancy between the internal flows from animal to crop and from crop to animal may have several causes:

- The literature based (*i.e.*, average) heavy-metal contents of concentrates and roughage are too low for Cu and Pb and too high for Cd and Zn;
- The literature based (*i.e.*, average) heavy-metal contents of animal (cow) manure are too high for Cu and Pb and too low for Cd and Zn;
- Significant Cu and Pb inputs may have been overlooked *e.g.*, from diffuse heavy-metal sources in extra feed additives, stable components and machinery, plumbing and water piping, soil ingestion, etc.;
- A combination of these three causes.

The heavy-metal contents in feedstuff and manure show large variations. Hence, it is risky to use averaged or literature values only. On-farm monitoring is needed to enable reliable on-site quantification.

Reiner *et al.* (1996) point to the possibilities to improve on-farm heavy-metal

management by checking metal inputs from diffuse sources *e.g.*, corrosion of piping. Soil ingestion may be important in the dietary intake of trace elements by grazing animals. For example, the size of this flow depends on grazing behavior, stocking density, soil type, weather conditions, season, length of the grass, and type of grass (Van Hooft, 1995). Where land is contaminated with elements of low availability to pasture, cattle may ingest up to 10 times the amount of the elements in the form of soil than that in herbage. Thus, the soil-animal flow may complement, or override the soil-plant-animal flow (Thornton, 1981). In the literature (Van Hooft, 1995) soil ingestion values from 100 to 900 (g d^{-1}), with a mean value of 427 ± 227, have been recorded. Lexmond (1992) stated that soil may comprise 1 (dry year) to 2% (wet year) of total dry matter intake. Thus, soil ingestion by animals and subsequent excretion in manure results in an internal cycle and internal redistribution of soil and metals.
Based on an average soil intake of 200 kg yr^{-1} and assuming heavy-metal soil contents at the Minderhoudhoeve similar to those at Nagele, the heavy-metal intake due to soil ingestion during grazing is ca. 100 mg, 5 g, 7 g, and 20 g for Cd, Cu, Pb, and Zn, respectively. Roughage, containing soil, may be another source of extra heavy-metal intake. However, heavy-metal intake from these sources does not account for the observed depletion of Cu and Pb. A combination of the possible causes for the discrepancies is therefore most likely.

Leaching
Reliable leaching data are both important and scarce. We derived adsorption models for the Nagele soil. For their interpretation, it is important to realize that the laboratory work does not resemble field circumstances exactly. For the Minderhoudhoeve systems, we used an average leaching rate based on literature values resulting in ranges of 0.5-2.8, 5-87, 4-35, and 2.6-88 g ha^{-1} yr^{-1} for Cd, Cu, Pb, and Zn, respectively. Using the extremes of these ranges instead of the average number, changes the balances significantly.

SSO-compost
Tables 6.12 and 6.13 show that the heavy-metal inputs associated with the use of SSO-compost are very high on the ecological mixed farm of the Minderhoudhoeve. The compost inputs were based on average values of heavy-metal contents in SSO-compost. If compost with higher or lower contents were used, the balances would differ significantly. Moreover, regular SSO-compost applications result in long-term changes in clay and organic matter contents which may considerably influence the heavy-metal contents in the course of time (Chapter 5).

Conclusions and recommendations

This study of heavy-metal balances in different agro-ecosystems in the Netherlands shows different heavy-metal input, output and accumulation patterns for different metals among and within the farming systems. Hence, specific analyses for each farming system are needed in addition to studying the total agricultural sector, as performed by statistical offices (*e.g.*, Van Eerdt & Stiggelbout, 1992).

Experimental farms are valuable resources for studying heavy-metal flows by measuring metal transfers at these sites. Integral monitoring of mineral, biocide, and heavy-metal flows at the farm gate is recommended to define options for developing sustainable management of agro-ecosystems.

Field-scale balances enable field specific and dynamic analyses of heavy-metal accumulation, leaching and uptake, and allow identification of 'hot spots' (*e.g.*, specific fields, crops, applications). Moreover, analyses on field scale enable elucidation of the role of internal cycles and quantification of soil-bound flows like dirt tare and erosion. The 'total field balance' really does not exist for mixed farms considering the differences between grassland and arable land. If large differences exist among fields due to individual treatments or specific processes, large discrepancies may be expected between farm-gate and field-scale balances.

An important issue in heavy-metal balance research is the lack of suitable methods to quantify leaching from the plough layer. Samples from drains do not reflect the situation just below the plough layer. Information from adsorption experiments is difficult to extrapolate to field situations and is not related to the actual water flux. This also holds for pore water analyses, which moreover only give an instantaneous impression of solute concentrations. Concurrent measurement of solute concentration (proportional solute sampling) and water flux just below the plough layer (water retention characteristics) would result in the most reliable leaching data.

Mixed farming systems compare favorably with specialized (arable or dairy) farming systems with regard to heavy-metal accumulation. Due to the internal cycling of forage and manure, less external inputs are required and thus import of heavy-metal containing raw materials and products is minimized. Mixed farming need not be restricted to farm level. Optimization of material use and minimization of waste production may be enhanced by 'mixed farming' on a regional scale. In that case, different types of enterprises (agricultural, industrial, recycling) should collaborate strategically to use effluents of one process as input for another.

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CHAPTER 7

HEAVY-METAL BALANCES OF AN ITALIAN SOIL AS AFFECTED BY SEWAGE SLUDGE AND BORDEAUX MIXTURE APPLICATIONS

Abstract

Applications of sewage sludge and Bordeaux mixture (a mixture of copper sulphate and lime) add heavy metals to the soil. At an experimental farm in the Cremona district (Italy), we measured current heavy-metal contents in soil and their removal via harvested products. We also measured heavy-metal adsorption by soil from this farm. With these data, projections were made of the long-term development of heavy-metal (Cd, Cu, Zn) contents in soil, crop removal and leaching at different application rates of sewage sludge and Bordeaux mixture. These projections were compared with existing quality standards of the European Union and Italy with regard to soil and groundwater. The calculations reveal that the permitted annual application rates of sewage sludge and Bordeaux mixture are likely to result in exceedance of groundwater and soil standards. Sewage sludge applications, complying with the Italian legal limits, may pose problems for Cd, Cu, and Zn within 30, 70, and 100 years, respectively. Furthermore, severe Cu pollution of integrated (mildew controlled by Bordeaux mixture and organo-pesticides) and especially organic (Bordeaux mixture only) vineyards is unavoidable with the currently allowed application rates of Bordeaux mixture. The results suggest that the current Italian soil protection policy as well as the European Union policy are not conducive of a sustainable heavy-metal management in agro-ecosystems.

Introduction

Prevention of heavy-metal accumulation in the soil is a prerequisite for sustainable agricultural production (Witter, 1996). The goal of reaching a 'sustainable balance' is hindered by large diffuse metal inputs from a combination of both natural and anthropogenic sources. Because only the latter are manageable, these should be minimized (McGrath *et al.*, 1994).
A predictive model for the long-term behavior of heavy metals in agricultural soils requires information on long-term trends in heavy-metal inputs from different sources, on changes in soil, crop and climatic conditions and on the behavior of heavy metals in soil-crop systems under different (climatic) conditions. Since it is impossible to develop this kind of models due to complexity and uncertainties involved, Harmsen (1992) developed a model with a limited number of parameters that demonstrates the consequences of certain basic assumptions about heavy-metal behavior in agricultural soils. In that sense, the patterns of behavior represented in the dynamic relations among variables are more important than actual values of the variables. This approach (*i.e.*, 'projection') is fruitful because it enables calculation of possible future developments. Also, it shows what data are needed to fill in gaps in current knowledge. Improving system understanding and predictive ability requires integration of model development, field and laboratory experimentation, and performance monitoring of the system studied (Jakeman *et al.*, 1993).
In this paper, we combine data from field and laboratory experiments as input for calculating heavy-metal balances with a dynamic model. Based on these projections, we address the question whether or not adverse effects due to heavy metals are to be expected for soil, crop and groundwater quality with currently allowed application rates of sewage sludge and Bordeaux mixture (a mixture of copper sulphate and lime) in Italy. The experimental farm chosen for this research is located in the area of Pieve S. Giacomo, a small village in the Cremona district, in the middle of the Po valley (45°1′ N, 10°1′ E). It is one of three experimentals farms where the effects of sewage sludge applications on soils are monitored.

Materials and Methods

With the dynamic balance equation for the plough layer (Eq. 4.10) it is possible to determine whether or not problems are likely to occur and, if so, for which metal, in which compartment (soil, produce or groundwater) and on which time-scale. General soil characteristics and heavy-metal contents were determined for the soil of the experimental field (Table 7.1). The total contents (G) were determined by *Aqua regia* digestion of 1 g of soil in 15 ml HNO_3-HCl mixture for 5 hours and subsequent additions of H_2O_2. The labile heavy-metal fraction (G_l) was determined with nitric acid (0.43 mol l^{-1} HNO_3), according to Houba *et al.* (1995). The heavy-metal contents agree with common values for the region.

Table 7.1. Main soil parameters for Pieve S. Giacomo experimental farm.

Clay; <2µ (%):	22.3	
Silt; 2-50µ (%):	62.6	
Sand; >50µ (%):	15.1	
Organic matter (%):	1.84	
ρ (kg m^{-3}):	1500	
pH-H_2O:	7.6	
CEC ($cmol_c$ kg^{-1}):	20	
	Aqua regia (G)	nitric acid (G_l)
Cd (mg kg^{-1} DW):	1.0 ± 0.12	0.43
Cu (mg kg^{-1} DW):	29.4 ± 1.8	13.6
Pb (mg kg^{-1} DW):	19.3 ± 3.3	17.2
Zn (mg kg^{-1} DW):	96.0 ± 10.4	24.8

DW: dry weight

To compare the effect of different heavy-metal inputs to the same soil we calculate dynamic heavy-metal balances based on two practices which are common in Italy, *i.e.*, applications of sewage sludge and applications of Bordeaux mixture.

The solution of the differential balance equation (Eq. 4.10) is approximated numerically using the 4th order Runge-Kutta method (Press *et al.*, 1986). Relatively small inputs like atmospheric deposition and fertilizer applications are neglected and all calculations are based on the soil properties of the experimental farm.

Input rate (A)

Sewage sludge:

In Italy, sewage sludge applications are regulated by Legislative Decree, which is based on a European Communities Council Directive (Table 7.2).

Table 7.2. Legislation regarding sewage sludge applications in agriculture.

	Cd	Cu	Pb	Zn
maximum metal contents in sewage sludge (mg kg^{-1} DW)				
European Union	20-40	1000-1750	750-1200	2500-4000
Italy	20	1000	750	2500
maximum permitted contents in agricultural soils with pH 6-7 (mg kg^{-1} DW)				
European Union	1-3	50-140	50-300	150-300
Italy	1.5	100	100	300
maximum average rate of addition (kg ha^{-1} yr^{-1})				
European Union	0.15	12	15	30
Italy	0.1	5	3.75	12.5

Sources: C.E.C., 1986 (EU) & Anonymous, 1992b (Italy); DW: dry weight.

In the period 1992-1996, the experimental field received 5 applications (one every year) of sewage sludge that were agronomically acceptable for the average crop requirements in the area (on average 3.54 ton DW ha^{-1} yr^{-1}). By multiplying this amount of sewage sludge by the average heavy-metal contents in the sludge during

1992-1996 (provided by pers. comm. with the Lombardy region sludge managers: Cd; 2.95, Cu; 572, Pb; 166, Zn; 1213 mg kg^{-1} DW), the heavy-metal additions to the soil of the experimental field are obtained (Table 7.3). The 'maximum average rate of addition' shown in Table 7.2 is used for the calculations related to the heavy-metal inputs according to Italian and EU limits (Table 7.3).

Bordeaux mixture:
The input of Cu with $CuSO_4$ in Bordeaux mixture (Bm) is estimated from the average numbers of Bm applications in 11 'integrated' and 'organic' vineyards in Reggio Emilia for which the total number of interventions (generally 10-12) and the quantities spread were determined in 1992 and 1993. The organic vineyard is protected against mildew (*Plasmopara viticola)* by the use of Bm only. The integrated vineyard uses a defense strategy with both organo-pesticides and Bm. The Cu additions in both types of vineyard are shown in Table 7.3.

Table 7.3. Total heavy-metal input (A: g ha^{-1} yr^{-1}).

	Cd	Cu	Pb	Zn
Sewage sludge:				
Exp. farm	10.4	2025	590	4293
Italian limit[1]	100	5000	3750	12500
EU limit[2]	150	12000	15000	30000
$CuSO_4$:	Cu			
Organic vineyard[3]	26000 (range: 15000-49000 on 3 farms in 1992 & 1993)			
Integrated vineyard[3]	10000 (range: 3000-16000 on 8 farms in 1992 & 1993)			

Sources: 1. Anonymous, 1992b; 2. C.E.C., 1986; 3. Anonymous, 1995.

In all calculations, the input rate (A) is considered to be constant in time.

Leaching rate (L)
Surface runoff is disregarded here because the experimental fields are level. Heavy-metal leaching down the profile may be enhanced by preferential (bypass) flow through soil cracks. Here, bypass flow is not taken into account and leaching is calculated as the product of the net precipitation (rainfall minus evapotranspiration) and the heavy-metal concentration in solution (Eq. 4.7). For the determination of the net precipitation we assumed a constant net infiltration rate (θv) of 0.2 m yr^{-1}, which is reasonable for this region. The plough layer thickness (l_p) equals 0.3 m.
The adsorption parameter values (k_f and n) were assessed for the (sludge-treated) soil of the experimental farm by measuring adsorption isotherms in batch experiments at soil pH (pH-$CaCl_2$ = 7.25) with 0.01 mol l^{-1} $CaCl_2$ as a background electrolyte. We carried out single metal adsorption experiments (each metal added separately) and combined metal adsorption experiments (metals added in a mixture of Cd, Cu, Pb, and Zn) to find out if any effects of competitive adsorption could be determined. Three g of air dried soil was mixed with 30 ml of 0.01 mol l^{-1} $CaCl_2$ solution (*i.e.*, soil:solution ratio of 1:10). The metal salts were dissolved in the 0.01

mol l^{-1} $CaCl_2$ solution and the soil suspensions were shaken end-over-end for 20 hours at 20 °C. After centrifuging the suspension for 15 minutes at 10000 ***g***, Cd, Cu and Pb were measured with Graphite Furnace Atomic Absorption Spectrometry (GFAAS) at 228.8 nm, 324.7 nm, and 217 nm, respectively. Zinc was measured with Flame Atomic Absorption Spectrometry (FAAS) at 213.9 nm. For further details we refer to Houba *et al.* (1995).

The heavy metals were added within a realistic concentration range. The single adsorption isotherms were measured for concentrations ranging from 0-0.25, 0-10, 0-10, 0-30 (mg l^{-1}) added in ten steps for Cd, Cu, Pb and Zn, respectively. In this way, the largest quantity added for Cu, Pb, and Zn corresponds with the Italian legal limit for soil (1.5, 100, 100, 300 mg kg^{-1} for Cd, Cu, Pb and Zn, respectively). For Cd, a larger amount (2.5 mg kg^{-1} soil) was added to make sure that the solution concentration would be above the detection limit.

The mixed adsorption isotherms were measured for concentrations ranging from 0-0.05, 0-10, 0-2.5, 0-20 (mg l^{-1}) added in 10 steps for Cd, Cu, Pb and Zn, respectively. The ratio between these metals approximately corresponds with the heavy-metal input ratio due to sewage sludge applications at the experimental farm (1: 200: 50: 400 cf. Table 7.3). Cadmium was used as a reference (maximum of 0.5 mg kg^{-1} added) and the other metals were added according to their ratio (maximum of 100, 25, 200 mg kg^{-1} added for Cu, Pb and Zn, respectively).

For Pb, no detectable concentrations (< 16 μg l^{-1}) could be measured in the equilibrium solution and hence no adsorption isotherm could be constructed. Therefore, in the remainder of this paper we will not further consider Pb. For Cu, a linear relationship between c and q was observed, while for Cd and Zn the adsorption isotherm could be well described with a Freundlich equation. Table 7.4 shows the results of the single and mixed adsorption experiments. The adsorption isotherms of Cd and Zn are characterized by the Freundlich parameters n and k_f which were determined after linearisation by logarithmic transformation.

Table 7.4. Adsorption isotherms. Solute metal concentration c (mg l^{-1}), amount of adsorbed metals q (mg kg^{-1}), and Freundlich parameters n and k_f (mg^{1-n} l^n kg^{-1}).

	Single adsorption			Mixed adsorption		
Freundlich adsorption	n	k_f	r^2	n	k_f	r^2
Cd	0.47	11.1	0.96	0.17	2.4	0.95
Zn	0.34	463.3	0.98	0.37	400.5	0.98
Linear adsorption:	Single adsorption		r^2	Mixed adsorption:		r^2
Cu	$q = 8.4\ 10^3c$		0.85	$q = 5.8\ 10^3c$		0.97

These results show that the adsorption behavior in the single metal experiments as compared to the combined metal experiments differs considerably for Cu and Cd. By substituting the adsorption parameters from the mixed-metal adsorption experiments in Eq. 4.7, the leaching rates after sewage sludge additions are determined. Results of the single-metal (Cu) experiments were used for the Bm calculations.

Crop removal rate (U)

Yield (Y) and tissue concentration (c_p) of colza (*Brassica napus* L.) and maize (*Zea mays* L.) were measured at three experimental farms in the same region in 1994 by Boccelli *et al.* (1997). Referring to Eqs. 4.8 and 4.9, we calculated uptake rate coefficients (B) for Cd and Zn that were based on these measured numbers by assuming a linear uptake relationship (m=1). The labile contents (G_l) are given in Table 7.1 and this content is expressed in mg m^{-3} by multiplying with the soil bulk density (ρ, Table 7.1).

For Cu, a constant removal rate is assumed since exclusion of Cu uptake may be operative (Mengel & Kirkby, 1982). Jarvis (1981) stated that over a wide range of total contents in a range of soils there is little relationship between Cu concentrations in soils and those in plants. Van Luit & Henkens (1967) found that there was no further increase in Cu content in perennial ryegrass (*Lolium perenne* L.), red clover (*Trifolium pratense* L.) and herbage after a Cu level of 5 mg kg^{-1} (Cu-HNO_3) was reached in different humic sandy soils. In case of the 'removal rate' by grapes (*Vitis vinifera* L.) it has to be noted that most Cu removed by grapes actually resembles the amount of Cu deposited on the grapes (resulting from the spreading of the Bm) and hence is not related to uptake by the vines. Since for Cu a constant removal rate is assumed for colza and maize, a direct comparison with the constant removal rates by grapes can be made (Table 7.5).

Table 7.5. Crop yield (Y) and tissue concentration (c_p).

c_p (mg kg^{-1} DW)[1]	Cd	Cu		Zn
Colza	0.01	3.6		36.5
Maize	0.01	1.8		18
Silage maize	0.08	5.2		21.7
Grape[2]		7		
Y (kg m^{-2} DW)[1]	Colza	Maize	Silage	Grape[2]
	0.34	1.1	3.3	1.2
Uptake rate B (10^{-4} yr^{-1}):	Colza	Maize	Silage	
Cd	0.17	0.68	14	
Zn	11	18	64	
Removal rate (g ha^{-1} yr^{-1}):	Colza	Maize	Silage	Grape[2]
Cu	12.2	20	171	83.5

Source: 1. Boccelli *et al.*, 1997; 2. Grape expressed on fresh weight: Anonymous, 1995.

Potential depressive effects on crop yields due to excessive heavy-metal uptake are not regarded.

Results

Five scenarios are studied:

- sewage sludge applications according to current rates on the experimental farm;
- maximum sewage sludge applications according to Italian regulations;

- maximum sewage sludge applications according to EU regulations;
- applications of Bordeaux mixture on an integrated vineyard;
- applications of Bordeaux mixture on an organic vineyard.

First, we show the effect of normal sludge applications at the experimental farm on heavy-metal accumulation in soil, concentrations in leachate, and contents in colza and maize. Then, we compare these outcomes with the results of addition rates which are allowed for by Italian and EU legal limits. Finally, a comparison is made between the accumulating effect of Cu according to these limits for sewage sludge on one hand and Bm applications in organic and integrated vineyards on the other.

Case I. Experimental farm results

The results for maize are derived in two ways. In the first approach, only the maize grain (corn) is taken off the field and the other parts of the maize plants are returned as straw. In the other approach, the whole maize plant is harvested to be used as animal feed (silage maize). In all cases, a gradual increase in total soil content, amount leached, and crop removal is predicted to take place as shown in Table 7.6.

Table 7.6. Total soil content (mg kg^{-1}), leaching (mg m^{-3}), and crop uptake (mg kg^{-1} DW) of Cd, Cu and Zn at t=0 and t=300 (yr) according to the dynamic balance calculations.

	Colza		Maize kernel		Silage maize	
time (yr)	0	300	0	300	0	300
Cd:						
Content	1	1.5	1	1.5	1	1.4
Leaching	0.05	3.98	0.05	3.87	0.05	1.58
Uptake	0.01	0.02	0.01	0.03	0.08	0.15
Cu:						
Content	30	162	30	162	30	152
Leaching	2.9	25.7	2.9	25.6	2.9	23.8
Constant uptake	3.6		1.8		5.2	
Zn:						
Content	100	324	100	302	100	204
Leaching	0.7	283.3	0.7	220.7	0.7	48.4
Uptake	36.5	367.9	18	164.6	21.7	112.6

Silage maize has the largest removal of metals which results in the slowest soil accumulation and consequently lower leaching rates. Due to this 'normal agricultural practice', soil contents of Cu will be exceeded first (after 160 years for colza and maize; after 170 years for silage maize), followed by soil contents of Zn (260 years for colza and maize) and Cd (300 years for colza and maize).

Table 7.6 shows that the differences between colza and maize kernel with regard to soil contents and leaching rate are very small and we only consider colza and silage maize for further comparisons.

Case *II. Comparison with Italian and EU legal limits*

Assuming sewage sludge application rates that are maximally allowed for by Italian (I) and EU regulations (Table 7.2), the balance calculations were carried out for colza and silage maize. Standards for groundwater and drinking water, according to Italian limits, are given in Table 7.7. Also the Dutch legal limits for groundwater of a 'standard soil' that is considered to be uncontaminated (target value) and seriously contaminated (intervention value) are shown for comparitive reasons. Based on these numbers, we have chosen 5, 100 and 1000 ($\mu g\ l^{-1}$) as appropriate groundwater limit values in Lombardy region for Cd, Cu, and Zn, respectively.

Table 7.7. Standards for groundwater concentrations ($mg\ m^{-3}$).

Legal limits:	Cd	Cu	Zn
Groundwater value (Lombardia)[1]	5-50	100-400	1000-4000
Drinking water limit (I)[2]	5	1000	3000
Groundwater target value (Dutch)[3]	< 0.4	< 15	< 65
Groundwater intervention value (Dutch)[3]	6	75	800

Sources: 1. Anonymous, 1996; 2. Anonymous, 1987; 3. Anonymous, 1990

The time needed, with these cropping systems, to exceed standards for both soil and leachate (*i.e.*, groundwater recharge) is shown in Table 7.8.

Table 7.8. Time needed (yr) to reach the groundwater and soil limit according to application rates of sewage sludge allowed for by Italian (I) and European (EU) limits.

	Groundwater limit:			Soil limit:		
Silage maize:						
	Exp. Farm	I	EU	Exp. Farm	I	EU
Cd	>300	26	17	>300	25	16
Cu	>300	>300	217	172	66	27
Zn	>300	>300	75	>300	108	31
Colza						
	Exp. Farm	I	EU	Exp. Farm	I	EU
Cd	>300	25	16	300	24	16
Cu	>300	>300	214	158	64	27
Zn	>300	158	60	258	77	35

At steady state, the soil Cd content is approximately 2 $mg\ kg^{-1}$ in all cases and the Cd concentration in leachate then equals ca. 50 $mg\ m^{-3}$ (I) or ca. 75 $mg\ m^{-3}$ (EU), which is higher than the highest allowed value according to limits of Lombardy Region (Table 7.7).

Figure 7.1 shows the progression towards steady state of the Cd soil content and of outputs by silage maize and leaching if maximum yearly applications according to Italian limits were to be continued. The 'filling-up index' (FUI) is defined as the quotient of the total soil content and the soil limit value. The rate at which this index reaches 1 shows the rate at which the limit value is being 'filled up' thus indicating the impact on soil quality.

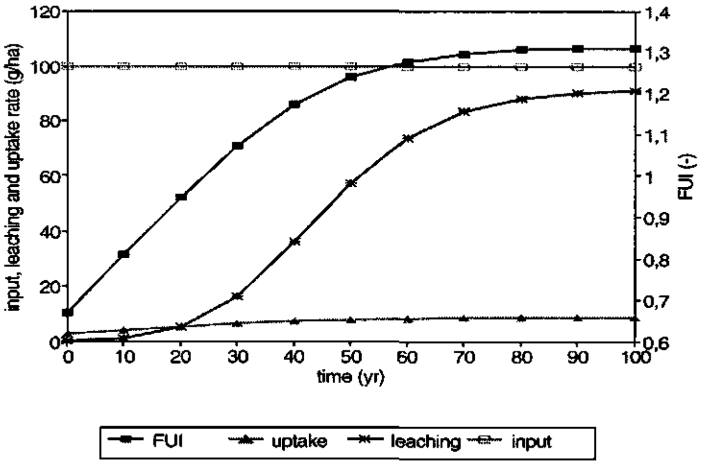

Figure 7.1. Cadmium input, leaching, uptake by silage maize, and accumulation in time due to maximum yearly sewage sludge applications according to the Italian legal limit. The Filling Up Index (FUI) equals the soil content divided by the soil standard.

Case III. Comparison of Bordeaux mixture additions and maximum allowable sewage sludge applications

In this comparison, we use the maximum application rates for sewage sludge according to Italian and EU regulations (case II). The outcomes of the calculations with silage maize are compared with the outcomes of the balance calculations for the organic and integrated vineyards with Bm additions only.

The amounts of Cu applied with Bm are shown in Table 7.3 and the comparison of the balance calculations with the limit values are given in Table 7.9.

Table 7.9. Time needed (yr) to reach the Cu groundwater and soil limits due to application rates in integrated (Bordeaux mixture and organo-pesticides) and organic (Bordeaux mixture only) vineyards.

	Groundwater limit (100 mg m^{-3}):		Soil limit (100 mg kg^{-1}):	
	Integrated	Organic	Integrated	Organic
Cu	>300 (90)[1]	139	31	13

1. The concentration (mg m^{-3}) that is reached after 300 years.

The consequences of continuing Bm additions in integrated and organic vineyards for Cu soil contents (Fig. 7.2) and leachate concentrations (Fig. 7.3) are compared with the outcomes due to the maximum allowable Cu additions with sewage sludge in Italy and the EU.

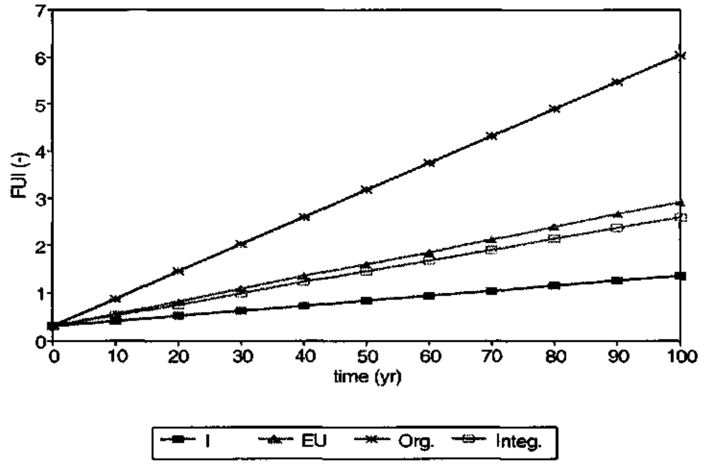

Figure 7.2. Filling Up Index (FUI: soil content divided by soil standard) for Cu in time due to Bm additions in integrated (Integ: Bm and organo-pesticides applications) and organic (Org: Bm applications only) vineyards compared with FUI values due to maximum allowable Cu additions with sewage sludge according to Italian (I) and EU limits.

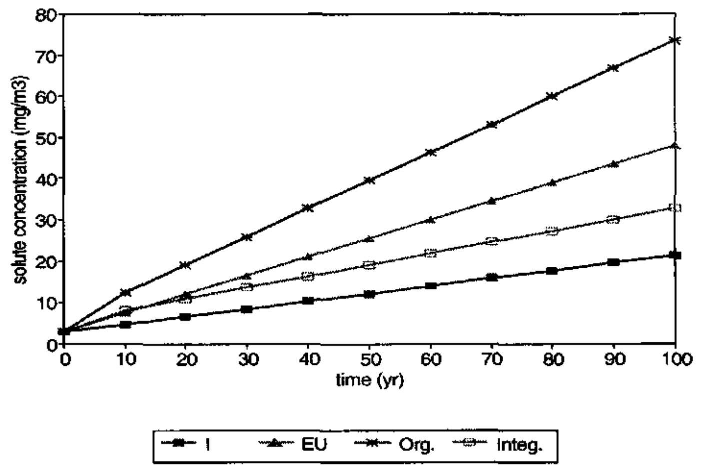

Figure 7.3. Copper concentrations in leachate in time due to Bm additions in integrated (Integ: Bm and organo-pesticides applications) and organic (Org: Bm applications only) vineyards compared with leachate concentrations due to the maximum allowable Cu additions with sewage sludge according to Italian (I) and EU limits.

Figure 7.2 shows that the organic vineyard management is least sustainable from a Cu contamination point of view. The Italian soil limit is exceeded within 10 (organic vineyard) to 70 (maximum Italian sewage sludge application rate) years for all allowed Cu additions.
Whereas the soil Cu content limits are exceeded within 100 years in all cases (Fig. 7.2), the Cu leachate concentrations do not exceed the groundwater limit value within 100 years according to the projections (Fig. 7.3).

Discussion

Sewage sludge is a useful source of mainly N, P, and organic matter. However, adverse effects of heavy metals added to the soil together with sewage sludge should be prevented. Our calculations show that currently allowed application rates of sewage sludge may lead to considerable Cd, Cu, and Zn accumulation. Kandeler *et al.* (1996) found that in heavy-metal contaminated soils, common biochemical properties that are necessary for the functioning of the ecosystem may be lost and they concluded that heavy-metal contamination severely decreases the functional diversity of the soil microbial community and impairs specific pathways of nutrient cycling. They suggested that heavy-metal contents in soils near the current EU limits lead to considerable reduction in decomposition of organic matter and nutrient cycling rates.
Organic amendments with high soil contents (like compost) may change the relative fractions of the soil constituents. In the case of applying soil amendments with high soil and/or organic matter contents it may therefore be important to account for the composition of both the soil amendments (the metal carrier) and of the soil itself when calculating heavy-metal balances. In the case of sewage sludge applications, the input of soil particles may be neglected but the input of organic matter is substantial. In our calculations, however, we did not take into account changes in soil composition due to organic matter additions, because the added organic matter decomposes rather quickly due to the relatively high temperature, the easily decomposable form in which the organic matter is present in sewage sludge, and yearly ploughing. In Italian soils without organic amendments organic matter levels generally decrease. On the experimental field, the organic matter contents have remained rather constant since sewage sludge applications started in 1992. Furthermore, since soil pH and organic matter content are expected to remain constant on this calcareous clay soil, no big changes in the uptake and leaching rates are expected. This justifies their being used as constants in the balance calculations.
With regard to the interpretation of the leaching numbers, it is important to notice that the adsorption experiments do not resemble the field circumstances. In balance studies, it is difficult to obtain proper leaching data. Leaching is therefore often neglected or estimations based on literature data are used. Here, we carried out adsorption experiments to determine the sorption properties of the soil of the experimental farm. Using the results of these experiments, metal adsorption and

leaching may be both under- and overestimated. The adsorption isotherms were determined with a 0.01 mol l^{-1} $CaCl_2$ solution as a background electrolyte. In this solution, the total dissolved metal concentration (including all metal complexes) is determined. Boekhold *et al.* (1993) found that in an 0.01 mol l^{-1} $CaCl_2$ electrolyte solution, 48% of the Cd ions were present in their free divalent cation form and the rest was complexed with Cl^-. Because only the Cd^{2+} species is able to adsorb in significant amounts, the presence of Ca and Cl may underestimate the amount of Cd adsorbed by the experimental soil. Although this has to be accounted for when interpreting the leaching data, Ca will be present in high concentrations in the soil solution of the experimental farm as well.

Furthermore, an important fraction of the total dissolved Cu in surface soils over a fairly wide range of pH (and particularly at higher pH) is in the form of Cu-organic complexes. Temminghoff *et al.* (1997a) found for a column study with a Cu-contaminated soil at pH 6.6 that more than 99% of the Cu in solution was complexed with dissolved organic matter (expressed as DOC). Thus, in the field, DOC may be very important for enhancing leaching. Also, in our soil the effect of organic complexation on solubility and leaching is expected to be very strong. If organic rich materials such as sewage sludge are land applied, almost all the dissolved Cu consists of soluble organic complexes which are less likely to readsorb in the subsoil than free Cu^{2+}. McBride *et al.* (1997) found that a large fraction of soluble Cu appeared to be in an organically complexed and mobile form on a field site that had received a single heavy application of municipal sewage sludge 15 years ago. They state that certainly for Cu, and probably for several other metals, any attempt to predict metal solubility or leachability as a function of soil properties must quantify the factors that affect organic matter solubility. Temminghoff *et al.* (1997a) found that the mobility of dissolved organic carbon was very sensitive to pH and calcium concentration. Decreased Ca concentration resulted in increased dissolved organic carbon concentration and the increase in Cu mobility due to DOC was larger at high pH than at low pH. In our experiments, Cu adsorption may be overestimated because Cu-DOC complexes in the field could enhance leaching to a large extent.

Bypass flow may result in a rapid downward migration of heavy metals and consequently higher concentrations in groundwater leachate and faster exceedance of limits than predicted here.

Bm has been used as a fungicide against mildew on grapevines in vineyards in France since 1855. The distribution of Cu in the soil profile is related to climatic, pedological, and agronomic conditions. Deluisa *et al.* (1996) found that most Cu in vineyards in the Plain Zone of Italy accumulated in the upper layers and also Flores-Vélez *et al.* (1996) found that after Cu is washed from leaves, shoots and grapes that have received Bm, it accumulates at the soil surface. Our calculations for the organic vineyard show that after 100 years the soil content increased up to 600 mg kg^{-1}. The accumulation of Cu at the soil surface and the planting of vineyards on slopes may favour its lateral transfer.

Undesirable accumulation in the food chain may occur if (fodder) crops were to be grown on the contaminated soil. For example, maize is used as a pioneer crop on former vineyards and the heavy-metal contents of silage maize may increase markedly in the future if amounts of sludge that comply with the Italian and EU limits are applied. Kirkham (1975) found on a sewage treatment farm in Ohio where sludge had been applied for 35 years that although heavy-metal levels were not increased in maize grain, concentrations of Cd and Cu in the leaves were higher than normal. So, if the maize were to be used for forage, then animals would be ingesting amounts of Cd and Cu that might be toxic. Jarausch-Wehrheim *et al.* (1996) studied the accumulation of sludge-borne Cu by field-grown maize and its distribution between the different plant organs. They found that the highest Cu concentrations in the upper maize leaves appeared at silage stage (*i.e.*, the last stage before maturity). Furthermore, microbial processes during ensilation might be affected because the microbial biomass is more sensitive to raised Cu concentrations than higher plants. Therefore, Jarausch-Wehrheim *et al.* (1996) recommend a regular analysis of the Cu concentration in those plant parts taken as fodder to detect possible detrimental effects in the food chain.

Because Bm is a protective agent, the Cu additions to grapes in vineyards (and to vegetable crops in the Mediterranean area) are much higher than the maximum allowed Cu additions with sewage sludge. National and European directives enhance the use of Bm for organic pest management. Lack of limits for the use of Bm makes coherent Cu management impossible and deserves reconsideration.

Conclusions and recommendations

The dynamic balance approach is a useful tool to compare the consequences of heavy-metal applications on agricultural land. Dynamic balance calculations can be carried out relatively simply if information is available about local application rates, soil and crop characteristics. The time-scale on which problems will occur is directly related to heavy-metal application rates. In the region studied, sewage sludge applications complying with the Italian legal limits pose problems for Cd, Cu, and Zn within 30, 70, and 100 years, respectively. With the currently allowed application rates of Bordeaux mixture, severe Cu contamination in integrated (Bordeaux mixture and organo-pesticides) and especially organic (Bordeaux mixture only) vineyards is unavoidable.

To validate the dynamic balance model and to gather relevant information for field-scale assessment of proper heavy-metal management, experimental research should focus on long-term monitoring of heavy metals in soil, crops, (groundwater) leachate, and on quantifying changes in heavy-metal uptake and sorption characteristics.

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CHAPTER 8

DYNAMIC COPPER BALANCES OF CONTAMINATED SANDY SOIL AS AFFECTED BY CHANGING SOLID AND DISSOLVED ORGANIC MATTER AND pH

Abstract

Changing land use from arable farming to forestry results in increasing soil organic matter content and H^+ solution concentrations. Effects of organic matter increase and pH decrease on Cu speciation and consequent Cu mobility are modeled for different land use change scenarios by incorporating the Two Species Freundlich equation in dynamic balances for Cu in soil. The land use change scenarios show that Cu accumulation in soil may appear harmless at first, but may adversely affect soil biology and groundwater quality later. Such effects depend on the Cu input history of the soil (agricultural use) and also to a large extent on the question whether the litter is mixed through the topsoil or not (forestry).

In a land use change scenario with high Cu input history, after 50 years, Cu leaching is about 4 times higher if the litter remains on top of the topsoil than in the cases of mixing litter through the topsoil or continuing high-input agriculture. The increase of the Cu^{2+} activity in the land use change scenarios as compared with continued agriculture (factor 30 and 750 for the mixed and non-mixed case, respectively) due to decreasing pH is apparent.

Introduction

Agricultural productivity in Europe is characterized by overproduction in relation to markets, considerable differences in productivity over the continent, and different potentials for increases in productivity under present technological conditions. Therefore, large areas of European agricultural land are being taken out of production according to 'set-aside' schemes (Brouwer *et al.*, 1991). An important land use change is changing arable land into forests. A majority of these forests are to be planted on soils with a relatively low potential for agricultural production. In the Netherlands, these areas consist largely of sandy soils with a low buffering capacity. 'The buffering capacity of soil with respect to soil contamination may be defined as its capacity to delay the negative effects of the contaminant's presence because of inactivation' (De Haan, 1996b). In case of changing land use, slow alterations gradually reduce the buffering capacity and predispose the system to adverse effects (Stigliani *et al.*, 1991).

Forestation will lead to a decrease in soil pH (due to termination of regular lime applications), an increase in the soil organic matter content (due to lower pH and and higher input of organic material without the removal of harvest products). Soil acidification is a natural process that can be strongly enhanced by atmospheric deposition of SO_2, NO_x, and NH_3. Soil acidification rates depend primarily on acid input rates and the soil acid neutralizing capacity. On a limed agricultural field that was later abandoned and converted into deciduous woodland, the pH of the plough layer decreased from pH 7 to 4.2 over 100 years (Johnston *et al.*, 1986). Hesterberg (1993) modeled changes in the solubility of some trace metals in soil as a result of acidification and found that zinc, cadmium and aluminum solubilities increased exponentially with decreasing pH and calcium concentrations after liming stops.

Soil organic matter (expressed as SOC; solid organic carbon) originates from decaying plant and animal products that have been converted to a more or less stable product (humus). Mineralization of organic matter and recycling of nutrients by plants is essential in the relationship between soil and the above-ground biosphere (Stevenson, 1982). Composition and turnover of organic matter have a profound bearing on the physical and chemical properties of the soil (Schulin *et al.*, 1995).

Accumulation of heavy metals in soil may cause problems if soil is to permanently fulfil its functions in agricultural production, in environmental processes, and as a habitat of numerous organisms. The biological availability and the mobility of heavy metals are controlled by their chemical speciation *i.e.*, the distribution of the total metal content over all possible chemical forms (species) that are present in the solid, the liquid, and the biotic phases of soil (Temminghoff *et al.*, 1997a). Adsorption of the 'free' heavy-metal ion on each soil component (soil particles, (in)organic ligands, biota) depends on factors like pH and competition. The 'free' metal ion fraction in the soil solution is often the most bioavailable fraction whereas heavy-metal complexes are often important with respect to mobility (Plette, 1996;

Temminghoff *et al.*, 1997a). Excess amounts of heavy metals may interfere with essential microbiological soil functions, like organic matter decomposition, nitrogen fixation, and nitrification. This may have substantial impacts on the entire ecological dynamics of soil. In turn, bioavailability of heavy metals in soil will strongly depend on biotic processes. Inhibition of litter decomposition tends to increase the storage capacity of heavy metals by SOC, because SOC may have a high (specific) binding capacity for heavy metals. If stable complexes of heavy metals and organic matter are formed, the toxic effect of these metals in contaminated acid soils may be reduced (Brümmer *et al.*, 1986). Decomposition of SOC may strongly affect the redox potential due to oxidation and the pH of the solution by producing organic acids and carbon dioxide. Through decomposition processes, dissolved organic matter (expressed as DOC; dissolved organic carbon) concentrations in the soil solution increase and these DOC compounds form soluble complexes with various heavy metals. In that way, the complexation of sorbed metal species by soluble organic ligands can enhance heavy-metal mobility (Häni *et al.*, 1996).

The extent to which heavy metals are mobile in an (acid) sandy soil depends on pH, the amounts sorbed by the SOC, and on the extent to which metal-DOC complexes are formed. Copper-DOC complexes are known to be important for enhancing Cu mobility and bioavailability in sandy soil (Temminghoff *et al.*, 1997a,b). Since the concentration of DOC may increase due to land use changes, the understanding of Cu-DOC binding is very important in this context (Temminghoff *et al.*, 1994).

In this chapter, we study the effect of increasing (solid and dissolved) organic matter and decreasing pH with regard to Cu accumulation and mobility in soil. For this purpose, the speciation of Cu and the consequent multi-phase competition (Cu complexation with SOC and DOC) are taken into account in dynamic Cu balances of the topsoil. In these dynamic soil balances, the organic matter dynamics influence the soil bulk density as well. In this way, we develop an integrated approach in which Cu speciation in solution is calculated with a well defined speciation model and incorporated in the dynamic soil balance.

We consider two extreme possibilities of how the system's boundaries develop after changing land use from arable farming to forestry. On the one hand, the fallen litter is considered to be mixed completely throughout the topsoil (*i.e.*, the former plough layer) by biological action (*e.g.*, earthworms, springtails, etc.). On the other hand, the same amount of organic matter as in the case of mixing accumulates on top of the soil by the formation of a litter layer, which is thus considered to be separate from the former plough layer. The Cu balances of the top 0.3 m (litter layer not taken into account) are compared for the two cases.

Theory

A balance of heavy metals in the topsoil relates the rates of change in heavy-metal content, input and output and can be given by:

$$\frac{dG}{dt} = A - L - U \qquad (8.1)$$

In equation 8.1, the change in total heavy-metal content in soil (dG/dt) depends on the input rate at the soil surface (A), the leaching rate at the lower boundary of the system (L) and the removal rate by harvesting plants (U). The topsoil is taken to be homogeneously mixed, which implies that the SOC and Cu contents do not show vertical variation within the system.

Leaching (L) and crop uptake (U) of heavy metals are related to the metal concentration in the soil solution which depends on sorption characteristics. Both empirical and semi-mechanistic models have been developed to describe heavy-metal adsorption by heterogeneous surfaces such as soil, (dissolved) organic matter and organisms. A semi-mechanistic Non-Ideal Competitive Adsorption (NICA) model was developed by Koopal *et al.* (1994). At median pH ranges and low heavy-metal concentrations the NICA equation can be simplified to a Two Species Freundlich equation (TSF) if only proton competition with one heavy metal is taken into account (Temminghoff *et al.*, 1997b):

$$Q_{Cu} = K'(Cu^{2+})^{n_{Cu}}(H^{+})^{m_H} \qquad (8.2)$$

Here, Q_{Cu} is the adsorbed quantity of Cu by organic matter (mol kg^{-1}), H^+ and Cu^{2+} are solute concentrations in mol l^{-1} and K′, n_{Cu}, and m_H are parameters that are quantified in Table 8.1.

Table 8.1. Parameters for the TSF model to describe copper binding by Dissolved Organic Matter (DOC) and Soil Organic Matter (SOC) at I=0.003.

	DOC	SOC
n_{Cu}	0.36	0.36
m_H	-0.40	-0.58
log K′	-0.348	-1.77

Source: Temminghoff *et al.* (1997b)

Temminghoff *et al.* (1997b) were able to describe both Cu binding by DOC and Cu binding by SOC with the NICA and the TSF model. At pH 3.9, about 30% of the total Cu in solution was complexed Cu-DOC. At pH 6.6, Cu-DOC comprised more than 99%. Furthermore, Temminghoff *et al.* (1997b) used both (NICA and TSF) models to *predict* the Cu concentration in the soil solution at different depths under

field conditions from the total Cu content, pH, SOC, and DOC contents.
We model the adsorption of Cu onto SOC and DOC with the TSF equation (Eq. 8.2) in the calculation of dynamic Cu balances in soil. Using the parameter values from Table 8.1, the distribution of Cu between SOC ($Q_{Cu\text{-}SOC}$; mol kg^{-1} SOC) and DOC ($Q_{Cu\text{-}DOC}$; mol kg^{-1} DOC) and free Cu^{2+} (mol l^{-1}) is calculated. The amount of adsorbed Cu on the soil solid phase ($Q_{Cu\text{-}soil}$; mol kg^{-1} soil) is derived from the amount of Cu adsorbed on SOC by accounting for the mass fraction of SOC (f_{SOC}):

$$Q_{Cu\text{-}soil}=f_{SOC}Q_{Cu\text{-}SOC} \tag{8.3}$$

The Cu-DOC concentration (mol l^{-1}) is related to $Q_{Cu\text{-}DOC}$ according to:

$$Cu\text{-}DOC=Q_{Cu\text{-}DOC}\ [DOC]\ 10^{-6} \tag{8.4}$$

where [DOC] is the DOC concentration in the soil solution (mg l^{-1}).
Using equations 8.2-8.4, the leaching rate (L) can be related to the total Cu concentration in the soil solution ($Cu_{sol} = Cu^{2+}$ + Cu-DOC):

$$L=\frac{\theta v(Cu_{sol})}{l_p} \tag{8.5}$$

where v is the pore water velocity (1 m yr^{-1}), θ is the volumetric water content of the soil (0.3 m^3 m^{-3}), and l_p is the plough layer thickness (0.3 m). Here, we consider only vertical solute transport. The values of θ, v, and l_p are taken to be representative for an 'average Dutch situation'.
Crop uptake rate is expressed here according to the relationship

$$U=BG^{m} \tag{8.6}$$

with the plant uptake rate coefficient (B) and total soil Cu content (G) (cf. Kuboi *et al.*, 1986). Based on Moolenaar & Lexmond (1998), we take m = 1 and B = 5 10^{-4} (yr^{-1}) for Cu offtake by an arable crop rotation. The solution of the differential balance equation (Eq. 8.1) is approximated numerically using the 4th order Runge-Kutta method (Press *et al.*, 1986).
Moolenaar *et al.* (1997b) developed a method for calculating heavy-metal balances, in which changes in soil composition are explicitly accounted for by calculating mass balances of heavy metals and of the main soil constituents at the same time. In this dynamic soil composition balance (DSCB) approach, the dynamics in soil composition are reflected in changing organic matter, clay and non-clay fractions of

the plough layer. These fractions determine the soil bulk density and hence the plough layer weight. The effect of changing SOC content on the soil bulk density (ρ: g m^{-3}) is modeled according to an empirical relation based on data gathered by Van Wijk & Beuving (1984):

$$\rho = \frac{1}{(0.6 + 3f_{SOC})} \tag{8.7}$$

The resulting Cu-soil content (expressed on unit mass: mmol kg^{-1}) is calculated by dividing the Cu content expressed on unit volume (mmol m^{-3}) by the new soil bulk density (kg m^{-3}) and by using a correction factor (*i.e.*, ρ_{new}/ρ_{old}) for constant plough layer thickness in the case of mixing. According to McBride *et al.* (1997), any attempt to predict Cu solubility or leachability as a function of soil properties must quantify the factors that affect organic matter solubility. We derived the relationship between DOC concentrations (mg l^{-1}), SOC content (%), and pH based on the measurements of SOC, DOC, and pH in a Cu contaminated sandy soil carried out by Temminghoff *et al.* (1997b). After logarithmic transformation, linear regression was carried out which resulted in the following equation:

$$\log(DOC) = 0.07 + 0.923\log(SOC) + 0.084pH \tag{8.8}$$

The correlation is good (coefficient of determination r^2 = 0.82) since important factors that determine the DOC concentration (*i.e.*, SOC and pH) are taken into account in this equation. The DOC concentration can be regulated by many factors like charge of DOC, binding onto metal (hydr)oxides and clay, and coagulation (Tipping & Woof, 1990). Therefore, extrapolation of Eq. 8.8 to other cases than the field used by Temminghoff *et al.* (1997b) should be carried out with caution.

In accordance with values measured by Johnston *et al.* (1986) and by Römkens & De Vries (1994), we assume that within 50 years after arable land is converted into forest the pH will decrease non-linearly from 6 to 4. This acidification pattern is simulated by a net yearly (linear) increase in the soil solution of 2 μmol H^+ per liter.

For all calculations it is assumed that arable farming or forestry are practised on the sandy soil which is described by Temminghoff *et al.* (1997b). The initial Cu soil content is 15 mg kg^{-1} (0.24 mmol kg^{-1}), which is a common value for Cu contents in Dutch sandy arable soil (Van Drecht *et al.*, 1997).

Scenarios

Three agricultural scenarios are defined to show different developments of soil Cu contents resulting from Cu input of manure and Cu output with crop offtake. One scenario serves as a 'base scenario' (*a*) because both Cu input and output by crop offtake are defined set equal to zero. The moderate Cu input (200 g ha^{-1}) scenario

(*b*) is based on application of cow manure. The high Cu input (800 g ha^{-1}) scenario (*c*) resembles the use of pig manure for continuous maize culture. Input rates for scenarios *b* and *c* are taken from IKC (1997). Agricultural scenarios (*a*-*c*) are assumed to have a constant pH (6) and SOC content (3%) resulting from management practices like liming, growing catch crops and manure applications.
After forestation, a situation where the litter is homogeneously mixed through the former plough layer by biological action and a situation where a separate litter layer is formed on top of the soil are distinguished. If mixing occurs, the SOC content of the topsoil increases linearly from 3-10% in 50 years. If a separate litter layer is formed, the SOC content remains constant (3%) whereas the newly formed litter layer is a source of fresh DOC input to the topsoil. Copper and SOC are assumed to remain uniformly distributed throughout the topsoil and the amount of DOC formed is equal in the mixed and non-mixed case. In the case of mixing litter through the topsoil, increasing SOC results in decreasing soil bulk density of the topsoil from about 1450 to 1100 (kg m^{-3}) in 50 years (according to Eq. 8.7). As a result of land use change, SOC, DOC and pH change as well. To quantify the effects of these changes separately, first calculations were carried out with increasing SOC (from 3 to 10%) at constant pH (*i.e.*, 6) in scenario *d* and with decreasing pH (from 6 to 4 in 50 years) at constant SOC content (*i.e.*, 3%) in scenario *e*.
Finally, in scenario *f*, agricultural practice with 100 years of high Cu inputs is followed by land use change with both decreasing pH and increasing SOC content during 50 years. Scenario *f* shows the changes in Cu speciation and accumulation for both the situation with and without litter being mixed through the topsoil.

Results

Agriculture
Figure 8.1 shows the development of Cu-soil content (mmol kg^{-1}) in agricultural scenarios *a*-*c*. In the scenarios with Cu input (*b* and *c*), the increasing Cu-soil contents show that the Cu input rates are higher than the respective sums of the leaching and crop offtake rates. In the case of moderate (200 g ha^{-1}) and high (800 g ha^{-1}) Cu input, the Cu-soil content increases from 0.25 to 0.28 and 0.49 mmol kg^{-1} after 100 years, respectively. Leaching losses in base scenario *a* are small as is shown by the very slow Cu depletion rate from 0.24 to 0.22 mmol kg^{-1} in this soil. Losses by leaching and crop offtake both increase from about 30 (g ha^{-1}) to 40 and 70 (g ha^{-1}) in 100 years in the moderate and high input cases, respectively.
The speciation of Cu in soil is calculated according to Eqs. 8.2 and 8.3. In the agricultural scenarios, the pH and SOC content remain the same and thus the amount of Cu adsorbed by SOC (Cu-SOC) increases with increasing Cu content in the soil and also the Cu-DOC concentrations follow the same pattern as the Cu-SOC contents. In the agricultural scenarios, the Cu-DOC concentrations are almost equal to the total amount of Cu in soil solution (Cu_{sol}) since > 99% of all Cu in solution is present as Cu-DOC.

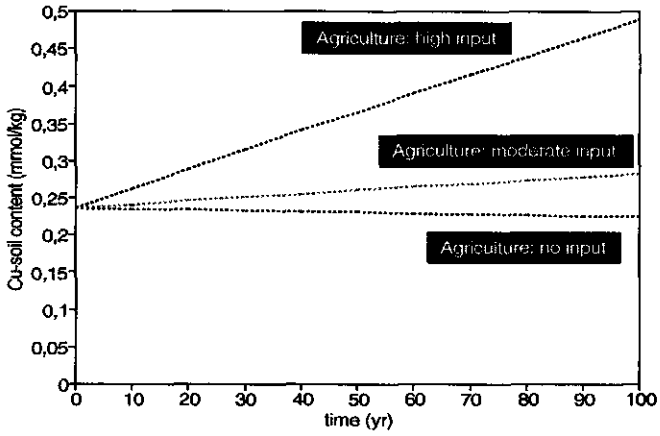

Figure 8.1. The development of the Cu-soil content in agricultural scenarios with high (800 g ha^{-1}), moderate (200 g ha^{-1}) and zero Cu input.

pH, SOC, and DOC changes

In the case of land use change, pH, SOC and DOC are subject to change. The SOC content of the topsoil increases linearly from 3-10% in 50 years. The developments of pH and DOC are shown in Figs. 8.2 and 8.3, respectively.

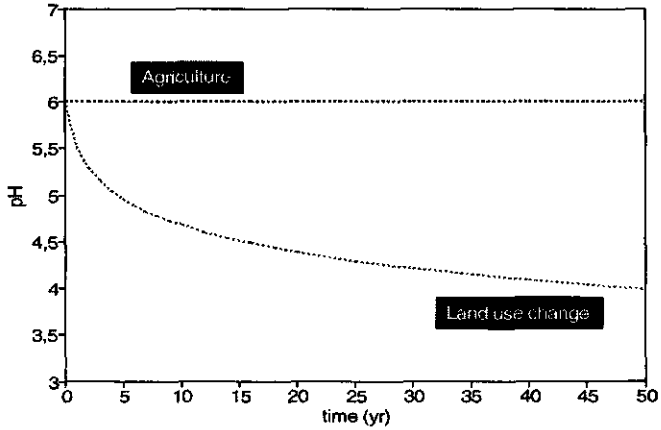

Figure 8.2. The development of pH during 50 years in the case of agriculture and land use change.

The DOC concentrations are calculated by substituting pH and SOC contents in Eq. 8.8. In the agricultural scenarios, SOC content and pH (Fig. 8.2) remain constant and so the DOC concentration remains constant as well (10 mg l^{-1}: Fig. 8.3). Due to the relatively fast pH decrease in the first 5 years after land use change (Fig. 8.2), the DOC concentration decreases at first and increases only after several years (due to increasing SOC content) up to 20 mg l^{-1} (scenario *f*). The case in which the pH remains constant with increasing SOC content (scenario *d*) results in the highest DOC concentrations (30 mg l^{-1}). If, at decreasing pH, the SOC content is kept constant (scenario *e*), the DOC concentration decreases to 7 mg l^{-1} after 50 years (Fig. 8.3).

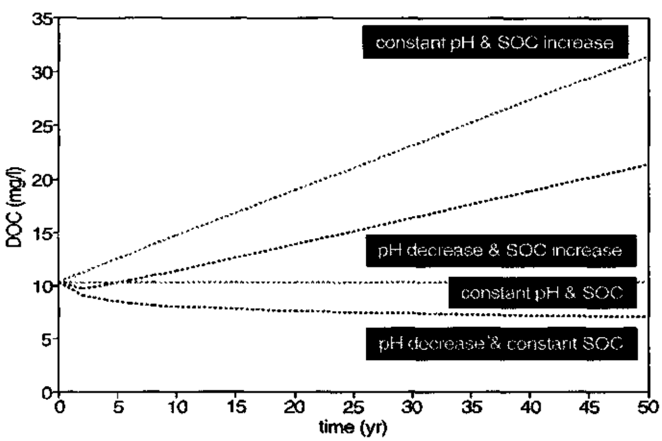

Figure 8.3. The development of the DOC concentration during 50 years in the case of constant and decreasing pH and constant and increasing SOC content.

Land use change

scenario *d*:

In the case of changing land use, litter falls on top of the former plough layer. First, agricultural base scenario *a* is compared with land use change scenario *d* in which the initial soil Cu content equals 0.24 mmol kg^{-1} (no Cu input history) and in which the pH is kept constant at 6. With these calculations the effect of increasing SOC are quantified. Figures 4a and 4b show the developments of the Cu-soil and Cu-SOC contents, respectively. In the mixed case, the SOC increases throughout the whole topsoil (0.3 m) and the Cu-soil content slightly differs from the situation where the litter remains on top of the soil (0.230 and 0.224 mmol kg^{-1} after 50 years, respectively) as is shown in Fig. 8.4a. In case of mixing, less Cu is available for leaching. The bulk of the amount of Cu present in soil remains adsorbed by SOC due to the constant pH value in this scenario. Therefore, the case of not mixing results in slightly lower Cu-soil contents. However, the Cu-SOC content in the mixed case decreases strongly (Fig. 8.4b). More SOC is available for Cu adsorption after mixing and thus Cu-SOC (expressed as mmol kg^{-1} SOC) is 'diluted' which is not the case if litter is not mixed.

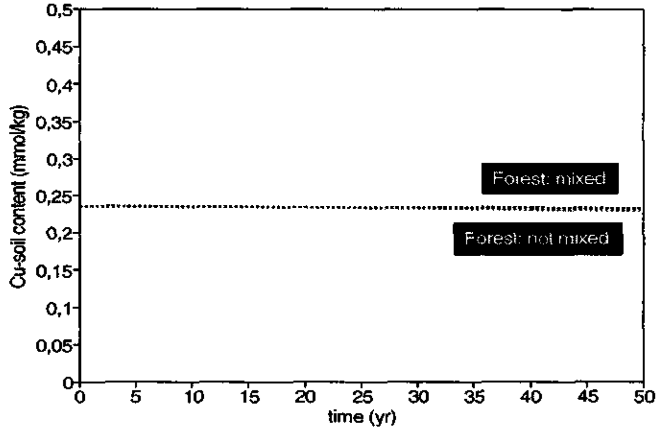

Figure 8.4a. The development of the Cu-soil content in the case of forestry (no Cu input history) with litter mixed and not mixed throughout the topsoil.

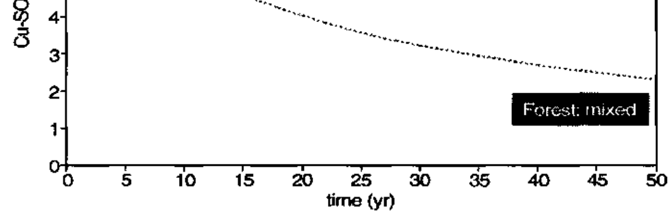

Figure 8.4b. The development of the Cu-SOC content in the case of agriculture and of forestry (no Cu input history) with litter mixed and not mixed throughout the topsoil.

Without mixing, scenario *d* results in slightly lower Cu-SOC contents than the

agricultural base scenario (Fig. 8.4b). Although the SOC content is the same in both cases, higher DOC concentrations are present in scenario *d* due to the litter layer.
Figure 8.4c shows that as a result of mixing the Cu solute concentrations do not increase as fast as in the non-mixing scenario, because due to mixing more binding sites on SOC are available. Consequently, the leaching rate is more than 3 times higher if the topsoil were not mixed compared with the mixed case after 50 years. The agricultural base scenario has the lowest leaching rate (Fig. 8.4c) and consequently the highest Cu-soil content (0.230 mol kg^{-1}) after 50 years.

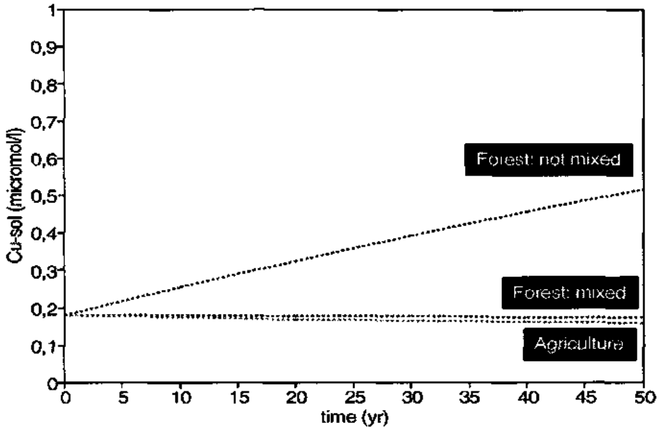

Figure 8.4c. The development of the total Cu solute concentration (Cu_{sol}) in the case of agriculture and of forestry (no Cu input history) with litter mixed and not mixed throughout the topsoil.

Because of relatively low DOC concentrations in the case of agriculture (Fig. 8.3), the Cu solute concentrations in the agricultural scenario are the lowest. In all three scenarios (*a*, *d* mixed, *d* not-mixed), 99% of the total Cu in solution is present in the form of Cu-DOC.

<u>scenario *e*:</u>
The Cu adsorption by SOC and consequently the Cu-soil content decrease slightly over time due to the effect of decreasing pH (6 to 4) and constant SOC content (3%) in scenario *e*. After 50 years, the Cu-soil content of scenario *e* still equals about 0.23 mmol kg^{-1}.
Due to decreasing pH, Cu solute concentrations (Cu_{sol}) increase almost two times compared with the case of constant pH after 50 years (Fig. 8.5). This is caused by Cu redistribution from the solid phase (Cu-SOC) to the solute phase (Cu-DOC and Cu^{2+}). In the scenario with decreasing pH, the percentage of complexed Cu-DOC in

the dissolved phase decreases from 99% to 87% in 50 years. The percentage of Cu^{2+} ions thus increases in the case of decreasing pH. The competition between H^+ and Cu^{2+} adsorption onto SOC and DOC determines the resulting Cu^{2+} concentration according to Eq. 8.2.

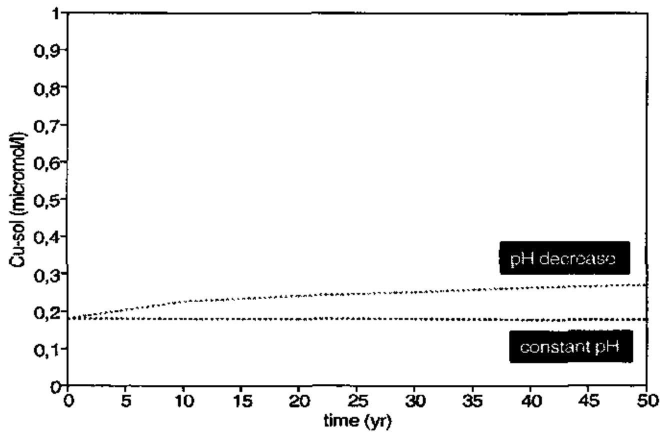

Figure 8.5. The effect of pH decrease on the development of the total Cu solute concentration (Cu_{sol}) in the case of forestry (no Cu input history) with constant SOC content.

<u>scenario *f*:</u>

Figure 8.6a shows the development of Cu-soil contents for the case in which first high-input agriculture is practised for 100 years and there after land use change occurs for another 50 years. The land use change scenario with a high-input history is studied for the situation that both the pH decreases from 6 to 4 and the SOC content increases from 3 to 10% in the case of mixing litter throughout the topsoil. If the litter remains on top of the soil, SOC content remains constant at 3%, but DOC increases up to 20 (mg l^{-1}) as in the mixed case.

During high-input agriculture, the Cu content increases from 0.24 to 0.49 mol kg^{-1}. If land use change starts, the manure inputs discontinue and the Cu-soil content decreases due to increasing leaching losses both in the case of mixing and non-mixing. However, Cu-soil decreases at a lower rate in the case of mixing (Fig. 8.6a).

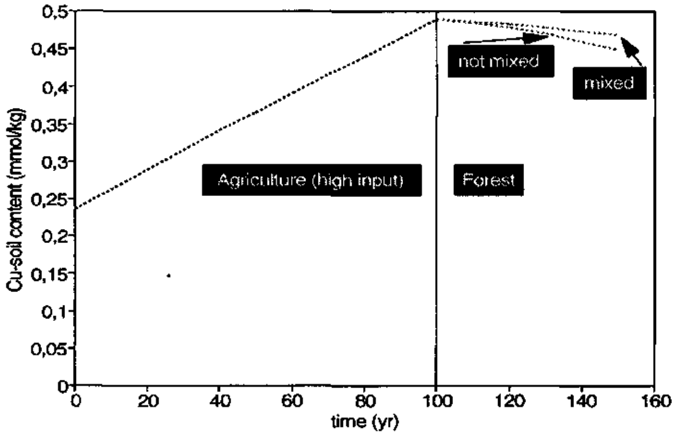

Figure 8.6a. The development of the Cu-soil content in the case of agriculture (high Cu input) followed by forestry with the litter mixed and not mixed throughout the topsoil.

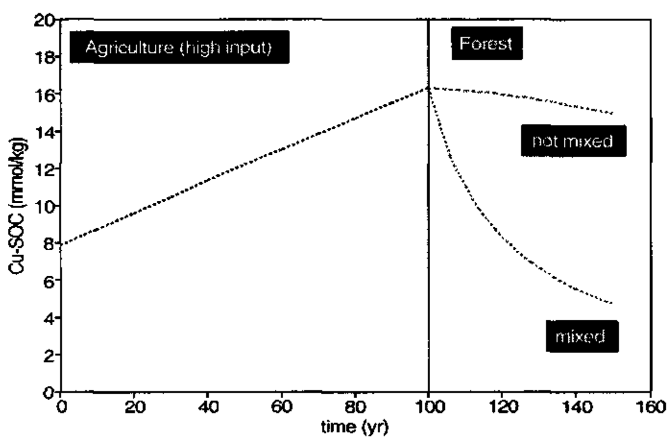

Figure 8.6b. The development of the Cu-SOC content in the case of agriculture (high Cu input) followed by forestry with litter mixed and not mixed throughout the topsoil.

With regard to Cu-SOC, the amount of Cu adsorbed onto SOC slowly decreases in the case of non mixing (Fig. 8.6b), because the Cu-soil content decreases at constant SOC content. The Cu-SOC content decreases much faster if mixing occurs because of 'dilution' of Cu-SOC.

In Figure 8.7, the mobile Cu concentrations are shown during 100 years of high-input agriculture and during 50 years if arable land were changed to forestry (with both pH decrease and SOC increase) in the case of mixing and not mixing.

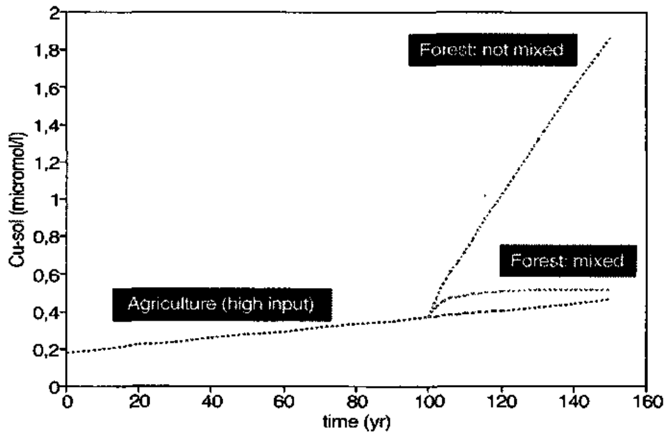

Figure 8.7. The development of the total Cu solute concentration (Cu_{sol}) in the case of agriculture (high Cu input) followed by forestry with litter mixed and not mixed throughout the topsoil.

In the case of agricultural land use, Cu-DOC comprises 99% of total Cu in solution. After land use change, the contribution of Cu-DOC to the total amount of Cu in solution (Cu_{sol}) is 86% in the non-mixing scenario and 98% in the mixing scenario after 50 years. At decreasing pH and increasing SOC content, the DOC concentration increases. Consequently, Cu-DOC concentrations increase. The combination with the more pronounced Cu redistribution from the solid phase to the solute phase in the case of not mixing results in higher Cu_{sol} concentrations. Due to land use change, the Cu mobility clearly increases and the value of Cu_{sol} after 50 years would be almost 1.1 (mixing) and 4 (non-mixing) times higher than if high-input agriculture were to be continued (Fig. 8.7). The pCu^{2+} (*i.e.*, $-\log[Cu^{2+}]$; mol l^{-1}) decreases from 9.72 at year 100 to 9.46, 7.99, and 6.59 at year 150 in the agricultural, the mixed, and the non-mixed case, respectively. These values are of the same order of magnitude as those found by Temminghoff *et al.* (1997b) at pH values 4 and 6. The large increase of the Cu^{2+} activity in the land use change scenarios as compared with continued agriculture (factor 30 and 750 for the mixed and non-mixed case, respectively) due to decreasing pH is apparent.
In the case of mixing, the Cu_{sol} concentrations start to decrease slowly after year 140 (Fig. 8.7). If the calculations would be continued, the Cu_{sol} concentrations of the agricultural scenario and of the mixed case would be the same at year 175. Continued agriculture results in increasing soil Cu contents (Cu_{sol} = 0.6 μmol l^{-1} at year

250) and hence in higher leaching rates than those occurring in the mixed case. The Cu_{sol} concentrations in case of non-mixing reach a maximum after about 230 year (at Cu_{sol} = 2.8 μmol l^{-1}) and the Cu_{sol}-concentrations decrease slowly afterwards.
At year 150, the Cu-soil content equals 0.61, 0.47, and 0.45 mmol kg^{-1} in the agricultural, the mixed, and the non-mixed case, respectively. Clearly, the Cu-soil content is lowest and the Cu leaching rate is highest in the case of land use change with a litter layer that remains separate from the rest of the topsoil.

Discussion and conclusions

By incorporating the Two Species Freundlich equation into a dynamic Cu balance of soil, it was possible to show the main effects of changing pH and soil organic matter (SOC and DOC) contents with respect to Cu speciation and the consequences for Cu mobility, bioavailability, and accumulation in a sandy soil after changing land use from arable farming to forestry.
In the case of continuing agriculture, groundwater quality will not be threatened at first. However, in that case the total soil Cu content may increase rapidly and the land use change scenarios showed that such accumulation may appear harmless at first, but may adversely affect soil biology (through increased uptake by soil flora and fauna) and groundwater quality (through increased leaching) later due to higher Cu availability and mobility. After land use change, the size and type of the heavy-metal flows change. Fertilization will stop but deposition may continue at higher rates due to different characteristics of the forest canopy compared with the arable crops. The input of Cu by deposition may thus not be negligible compared to the amount of Cu that is already present in the topsoil, as is assumed in this paper. Because the litter layer will be newly formed, we neglected Cu-DOC leaching from this layer in our calculations. Depending on the role of atmospheric Cu deposition (and subsequent foliar uptake and sorption onto leaves), the Cu input to the topsoil, its impact on distribution in the humus layer and the mineral soil profile, and subsequent leaching may be underestimated.
The organic matter dynamics show two extremes of how the soil organic matter content and the dissolved organic carbon concentrations might develop in the course of time in order to clarify the relative importance of mixing litter through the topsoil. The rate at which adverse effects may occur depends to a large extent on whether the litter is mixed through the topsoil by biological action or not. In the end, continuing high-input agriculture may result in more adverse effects (due to Cu accumulation and leaching) than changing to forestry where litter is mixed through the topsoil. The non-mixing situation was shown to result in the highest Cu concentrations in the soil solution. The calculations showed that the Cu_{sol} after 50 years would be 4 times higher while the Cu^{2+} concentration would be 750 times higher than if high-input agriculture would be continued.
These results show that speciation changes dramatically with far reaching consequences for mobility and bioavailability.

CHAPTER 9

INDICATORS OF THE SUSTAINABILITY OF HEAVY-METAL MANAGEMENT IN AGRO-ECOSYSTEMS

Abstract

The aim of sustainable heavy-metal management in agro-ecosystems is to ensure that the soil continues to fulfil its function in agricultural production, in environmental processes such as the cycling of elements, and as a habitat of numerous organisms. Assessment of sustainability has to be carried out in time, since metal accumulation in soil is largely irreversible and may cause problems if certain concentration levels are exceeded. In this study, we provide a concept to assess the sustainability of current metal cycles in agro-ecosystems based on dynamic heavy metal balances for the plough layer. After presenting some general aspects of dynamic metal balances we introduce 'sustainability indices'. These characteristic numbers can be used as indicators for potentially adverse effects of current agricultural practices, since they account for (ecotoxicologically founded) soil quality standards and for quality standards for produce, ground- and surface water. They can also be used to assess the effects of different management options that aim at preventing quality standards from being exceeded as they provide insight in the dynamics governing input-output relationships. This is illustrated with a case study on heavy-metal flows in different arable farming systems.

Introduction

'Sustainable agriculture' is, among others, related to environmental, agronomic, ethical, and socio-economic issues. One aspect of sustainability is the accumulation of heavy metals in soil, which can cause problems if certain concentration levels are exceeded (Alloway, 1995). The productivity of soil and quality of produce should be protected but at the same time the ecological functioning of the soil should not be damaged, nor should emissions from the soil adversely affect other environmental compartments. Therefore, prevention of heavy-metal accumulation is one of the prerequisites for sustainable agricultural production.

Two essentially different approaches exist to determine safe levels for burdening the terrestrial environment with potentially toxic, persistent compounds such as heavy metals. The first one is the risk approach that relies on maximum values for (total) metal contents in soil, which are derived from so-called no-observed-adverse-effect-concentrations (NOAEC's). The second one is the no-nett-degradation approach (NND approach), which is based on the precautionary principle aiming at no accumulation of possibly hazardous elements in the soil. Although both approaches emphasize that 'risks' have to be avoided, there is a fundamental difference in how this risk is perceived. This is related to differences in environmental priorities and in attitudes towards risk and risk aversion (McGrath *et al.*, 1994). The risk approach allows accumulation until a certain soil content is reached. The NND approach does not allow any further accumulation of persistent compounds in soil at all. The latter point of view recognizes the persistence of heavy metals as well as the need to preserve the agronomic value of soils (Witter, 1996).

In the Netherlands, it was shown that in some cases the current background values already equal or exceed ecotoxicologically derived maximum tolerable risk levels for heavy metals (Anonymous, 1991c). This means that also in the risk approach any further accumulation of certain metals should be avoided. For Cd, a heavy metal that poses a risk to human health, this is agreed upon internationally as well. The Joint FAO/WHO Expert Committee on Food Additives (JECFA) emphasized the small margin between Cd intake levels with the normal diet and intake levels that result in adverse effects to human health (JECFA, 1989). In fact, the provisional tolerable weekly intake (PTWI) for Cd is now considered to be insufficient to prevent the kidney from being damaged (JECFA, 1993). Further-more, it is important to realize that a situation without actual risks might cause severe risks in the future. The soil can act as a 'secondary source', which means that metals which initially are retained safely because of the soil's buffering capacity can be released due to processes that reduce the buffering capacity. These examples show that although the risk approach and the NND approach differ in theory, they will both aim at no further accumulation in practice.

However, 'zero accumulation' or 'no nett degradation' are not very manageable concepts to deal with in practice. The goal of reaching a sustainable balance thus preventing further accumulation can be impeded by large diffuse metal inputs from a combination of both natural (*e.g.*, vulcanic eruptions, forest fires and weathering from rock reservoirs) and anthropogenic sources (*e.g.*, waste incinerators, metal smelters, iron and steel factories). Since only the anthropogenic inputs are manageable, these should be minimized (McGrath *et al.*, 1994).

Soil quality standards that are based on metal contents in soil only, are of limited value because they do not reveal sustainable practices even if they are ecotoxicologically founded. Moreover, current standards for soil quality usually are not related to standards for (emissions to) other compartments. Effects depend on metal bioavailability (uptake by organisms) and chemical availability (leaching and mobility), which are related to many soil properties in a complicated way. The ecological effects of heavy metals in soils are closely related to both the concentration and the speciation of the elements in the solid and liquid phases of soils. Accumulation per se, as the primary effect of metal input exceeding output, does not indicate whether there is a problem. Bioavailability of heavy metals varies spatially and temporarily and determines the impact of accumulation on the ecosystem (effects on plants, animals and ecological processes) and its significance to man as secondary effects. Although soil quality standards are generally expressed in (total) contents it is therefore unsatisfactory to express 'good soil quality' in total contents only (Van Wensem *et al.*, 1994; Van Straalen & Bergema, 1995).

The search for more specific and quantifiable indicators of sustainable development has started quite recently (Kuik & Verbruggen, 1991; Adriaanse, 1993; Gilbert & Feenstra, 1994). Larson and Pierce (1994) stress that it is difficult to develop and evaluate sustainable management systems due to lack of (agreement on) credible measures of sustainability. Our aim is to provide a conceptual framework to assess the sustainability of current heavy metal cycles in agro-ecosystems.

We discuss the use of so-called sustainability indices as an extension of existing standards. These indices can be used as indicators of sustainable heavy-metal management in agro-ecosystems, since they provide insight in the relative importance of different heavy-metal flows. This allows priority assessment of protection measures and quantification of the gains of management options that aim at preventing standards for unacceptable risk (for soil, crop and groundwater) from being reached. The sustainability indices have been derived from a dynamic balance of heavy metals in soil and we illustrate the use of these characteristic numbers with a case study of four different farming systems.

The dynamic balance concept

A balance of heavy metals in soil relates the rates of accumulation, input and output and can be given by:

$$\frac{dG}{dt} = A - U - L = A - BG_l^m - CG_l^n \qquad (9.1a)$$

In equation 9.1a, the change in total heavy-metal content in soil (dG/dt: g m^{-3} yr^{-1}) depends on the labile fraction of the total soil content (G_l: g m^{-3}), the input rate at the soil surface (A: g m^{-3} yr^{-1}), the leaching rate at the lower boundary of the system (L: g m^{-3} yr^{-1}), and the removal rate by harvesting plants (U: g m^{-3} yr^{-1}). With this dynamic balance equation, soil contents can be calculated as a function of time, revealing if problems are likely to occur and, if so, for which element, in which compartment (produce or groundwater) and on which time-scale.

Two cases, *i.e.*, a linear (m=n=1) and a non-linear (m=1, n=1/2) balance equation will be studied for illustrative purposes. The values of the input rate parameter (A), plant uptake rate coefficient (B: yr^{-1}), and leaching rate parameter (C: yr^{-1} if n=1 and m^3 g^{-1} yr^{-1} if n=1/2) are assumed to be constants in both cases.

The linear balance

For m=n=1, the balance equation (Eq. 9.1a) becomes:

$$\frac{dG}{dt}=A-(B+C)G_l \qquad (9.1b)$$

It can easily be seen from Eq. 9.1b that (B+C) is equal to the 'elimination rate constant'. Integrating this balance, yields, for initial content G_0:

$$G(t)=\frac{A(1-e^{-(B+C)t})+(B+C)G_0e^{-(B+C)t}}{B+C} \qquad (9.2)$$

which reduces to a more simple form for negligible initial heavy-metal contents in soil (G=0 at t=0). The value of G at steady state (*ss*) is given by

$$G(ss)=\frac{A}{B+C} \qquad (9.3)$$

The non-linear balance

Often, non-linear adsorption isotherms are observed for heavy metals (De Haan *et al.*, 1987). The value of n in the case-study soil equals 1/2, which implies a strong non-linear adsorption behavior. Hence, for m=1 and n=1/2, the balance equation becomes:

$$\frac{dG}{dt}=A-BG_l-CG_l^2 \qquad (9.4)$$

Integrating this balance yields an analytical solution:

$$G(t)=\frac{2A(e^{t\sqrt{D}}-1)-(B-\sqrt{D})G_0e^{t\sqrt{D}}+(B+\sqrt{D})G_0}{2CG_0(e^{t\sqrt{D}}-1)-(B-\sqrt{D})+(B+\sqrt{D})e^{t\sqrt{D}}} \tag{9.5a}$$

with

$$D=B^2+4AC \tag{9.5b}$$

which reduces to

$$G(t)=\frac{2A(e^{t\sqrt{D}}-1)}{[(B+\sqrt{D})e^{t\sqrt{D}}-B+\sqrt{D}]} \tag{9.5c}$$

for negligible initial heavy-metal contents in soil (G=0 at t=0). For the non-linear balance, the value of G at steady state is given by

$$G(ss)=\frac{B-\sqrt{D}}{-2C} \tag{9.6}$$

Sustainability indices

In reality, the parameters related to plant uptake and leaching depend on many chemical, physical and biological properties of the soil-plant-system. The combination of a huge variety of soil properties and these chemical, physical and biological conditions makes the development of general rules for quantitative evaluation of soil quality a difficult task. Hence, the assessment of the heavy-metal balance for many different situations is often impossible as notably the plant uptake and leaching rate parameters may be difficult to quantify. Furthermore, a balance assessment at a larger scale may lead to wrong conclusions locally. Fortunately, characteristic numbers can be derived from the dynamic balance that either do not suffer from these shortcomings or that enable us to prioritize which limited data should be experimentally assessed in case commonly available data suggest that problems with regard to heavy metals should be anticipated. Using the input (A) and output (B, C) rate parameters, a quantitative evaluation of specific local situations and of characteristic 'general situations' can be carried out with the help of *sustainability indices*. These indices are based on existing or proposed quality standards and serve as indicators for adverse effects on the soil and related compartments. They are useful in view of the often limited availability of (reliable) data with respect to the soil-plant-system and input parameters that are needed to characterize an agro-ecosystem.

The discrepancy factor
At steady state, the accumulation rate equals zero and therefore

$$A = BG_l + CG_l^{1/n} \tag{9.7}$$

This means that the input rate equals the sum of the output rates. If we replace the output rates by the maximum acceptable output rates based on existing quality standards for crop and groundwater, we can define the *discrepancy factor* (F_d) for the soil compartment. This yields:

$$F_d = \frac{A}{U_c + L_c} \tag{9.8}$$

The discrepancy factor compares the input rate with the total acceptable output rate and as such is directly related with inputs (A) from agricultural and non-agricultural sources and with existing or proposed standards for acceptable crop quality (maximum acceptable removal rate by harvest: U_c) and groundwater quality (maximum acceptable leaching rate: L_c). If the discrepancy factor exceeds 1, problems are expected to occur since the input rate exceeds the sum of allowable output rates. By comparing the discrepancy factors for different metals we can assess which heavy metal will eventually lead to the largest violation of (groundwater or crop) standards, *i.e.*, which metal is relatively most 'abundant'. So, the power of F_d is that it allows for prioritization between different metals (De Haan & Van der Zee, 1993).
The value of F_d (Eq. 9.8) may underestimate the real discrepancy between input and acceptable output since it uses the summation of U_c and L_c. In practice, one of these two removal rates determines which heavy-metal input is still acceptable. Moreover, the discrepancy factor does not take into account any standards for soil ecology. Therefore, the value of F_d serves as a first indicator of potential problems only.

The critical sustainability factor
The discrepancy factor does not reveal whether problems are due with regard to soil, crop or groundwater quality. If limited data regarding water flow, heavy-metal sorption, mobility and bioavailability are available, a more advanced assessment is feasible. The ranking of the threat to the different compartments at steady state depends on which limit is exceeded most and can be assessed with the *sustainability factors* for ecology (F_e), crop uptake (F_u), and soil solution or leaching (F_s). Thus, the most threatened object may be identified by comparing the steady-state values of the soil content, the crop uptake rate and the leaching rate with the corresponding critical values. This is shown by the *critical* sustainability factor (F_c), given by

$$F_c = MAX(F_e, F_u, F_s) = MAX\left(\frac{G_{ss}}{G_e}, \frac{BG_{ss}}{U_c}, \frac{CG_{ss}^{1/n}}{L_c}\right) \tag{9.9}$$

which may be different for different heavy metals. G_e is an ecological soil quality standard that includes phytotoxicity to cultivated crops as well (*e.g.*, Van Straalen & Denneman, 1989).

The critical sustainability time

Whereas the above characteristic numbers do not yield information on the time when standards will be violated, for each threatened function expressions for these *sustainability times* can be derived from the dynamic balance (t_e: time at which the ecological quality standard is exceeded; t_u: time at which the crop quality limit is exceeded; t_s: time at which the groundwater limit is exceeded). The *critical* sustainability time (t_c) identifies the compartment for which the quality standard (G_e, U_c or L_c), if exceeded, is exceeded first and is thus defined as:

$$t_c = MIN(t_e, t_u, t_s) \tag{9.10}$$

A smaller value for U_c, L_c, or G_e, results in a smaller value for the respective sustainability times. In the linear case, t_e is given by

$$t_e = \frac{\ln \dfrac{[A-(B+C)G_0]}{[A-(B+C)G_e]}}{B+C} \tag{9.11}$$

The expressions for t_u and t_s can be found by replacing G_e in Eq. 9.11 by U_c/B and L_c/C, respectively. The same expressions can be used in the case of negligible initial heavy-metal contents by setting G_0=0. It is assumed here that G_0 is smaller than the critical G values and consequently that A (input rate) exceeds the sum of B and C during the accumulating phase. These equations show that the largest sustainability factor has the smallest sustainability time for the linear model. Hence, the compartment that is threatened most at steady state is also threatened first.

In the non-linear case, t_e is given by

$$t_e = \frac{\ln[\dfrac{2A-(B+\sqrt{D})G_0-(B-\sqrt{D}+2CG_0)G_e}{2A-(B-\sqrt{D})G_0-(B+\sqrt{D}+2CG_0)G_e}]}{\sqrt{D}} \tag{9.12}$$

The equations for t_u and t_s can be found by replacing G_e in Eq. 9.12 by U_c/B and $(L_c/C)^{1/2}$, respectively. By definition, a smaller value of U_c, L_c and G_e results in a smaller sustainability time. Observe that in the non-linear case $(L_c/C)^{1/2}$ does not equal the reciprocal of the sustainability factor as in all other cases. Due to non-linearity of the adsorption equation, the largest critical sustainability factor does not

necessarily correspond with the smallest sustainability time.
The advantage of using sustainability times and sustainability factors is that they are useful in comparing different systems. The calculation of these sustainability indices allows for a quick and efficient assessment of the information that is most relevant. Moreover, the results comply with the often limited data availability: a more specific analysis requires high quality input data. With the current generally available data it seems that the assumption of linearity is not the main constraint with respect to how realistic the approach is. As long as the standards for soil, groundwater and product quality are at best indicative of possible effects, relative criteria for sustainability as presented here may serve well for the purpose of classification and prioritization.

Case study: the sustainability of cadmium management in arable farming

In the case study on Cd management at the farm level it is shown how the concept of sustainability indices can be applied in real agro-ecosystems. We compare four arable farming systems: a conventional arable farming system, an integrated arable farming system and an ecological arable farming system. For the conventional system we distinguish two versions: one with the combined use of mineral and organic fertilizers (conventional-OF), and one with the exclusive use of mineral fertilizers (conventional-MF). These four systems are practised at an experimental farm at Nagele, the Netherlands. For a more detailed description of the farming systems, fertilizer use and crop rotations we refer to Vereijken (1992).
The farm is situated on a marine loam soil (ρ=1400 kg m^{-3}) with a mean total Cd soil content of 0.5 mg kg^{-1}, high pH (pH-KCl=7.3) and $CaCO_3$ content (10% by weight).
The rate parameters (A, B and C) largely determine the long-term soil contents and the value of the sustainability indices. The value of the soil content above which the crop quality limit will be exceeded (G_u: g m^{-3}) is very sensitive to the choice of the acceptable crop quality and to the value of the plant uptake rate parameter. In the case of crops with little uptake (*e.g.*, for barley), G_u-values could become very high if continuous cropping were practised. In the case of a continuous celeriac culture, hardly any accumulation would occur because of the high crop uptake rate involved in that case (Moolenaar *et al.*, 1996). Since continuous cultures are not realistic we focus on the entire crop rotation here.
The long-term behavior of Cd can be simulated using the mean area-weighted values of the input and output rate parameters for each entire farming system. The value of A (Cd input) is based on atmospheric deposition (assumed constant at 2 g ha^{-1} yr^{-1}) and fertilizer applications. The NK-fertilizers (CAN *i.e.*, NH_4NO_3+$CaCO_3$ and K-60) were practically free of Cd. Triple superphosphate (TSP) had a Cd content of 31 mg kg^{-1} with a Cd/P_2O_5 ratio of 68 mg kg^{-1}. The organic fertilizers (goat, cattle and poultry manure) had comparable contents of Cd. The Cd/P_2O_5 ratio of liquid poultry manure was 7.7 mg kg^{-1} while for goat and cattle manure the

corresponding ratios were 31 and 21 mg kg^{-1}, respectively.
The values of B and C were determined by Hatziotis (1995) according to Eqs. 4.9 and 4.11. The Freundlich parameters (n, k_f) have been based on Freundlich adsorption isotherms of a similar loam soil (soil no. 10 of De Haan *et al.*, 1987). The groundwater recharge rate is the product of the volumetric water content (θ) and the pore water velocity (v). In the average Dutch situation they equal 0.3 and 1, respectively. The plough layer thickness (l_p) is ca. 0.3 m.
The input parameters of the different arable farming systems are presented in Table 9.1. We assume that the Dutch reference value for the Cd content in this soil (*i.e.*, 0.59 mg kg^{-1}) equals the ecological quality standard (G_e). The value of U_c is the product of the yield (Y) and the quality standards of the crops involved. The value of L_c is the product of the quality standard for groundwater and the groundwater recharge rate. These values are related with corresponding (critical) soil contents for crop uptake and leaching (G_u and G_s, respectively) according to Eqs. 4.7 and 4.8. The groundwater quality standard has been based on the Dutch target value for the Cd concentration in groundwater, which equals 0.4 ($mg.m^{-3}$) (Anonymous, 1991c). The acceptable crop quality (U_c) is based on Dutch limit values for different crops (Anonymous, 1993). We took half the value of the crop quality standard as an acceptable value. This is preferable, since the chance of exceeding the crop standard is then likely to be less than 5% (Ferdinandus *et al.*, 1989). The U_c-value was not calculated as an area-weighted mean, because there are no limit values for all the crops involved. The U_c-values for different crops in the crop rotations varies between 1.10^{-3} and 1.10^{-4}. Hence, for some crops the 'average' limit value of 5.10^{-4} is low and for others it is high.

Table 9.1. Input parameters of four arable farming systems.

Input:	Ecological	Integrated	Conventional-OF	Conventional-MF
n	0.5	0.5	0.5	0.5
$k_f (g^{0.5}\ m^{1.5}\ kg^{-1})$	0.072	0.072	0.072	0.072
A ($x10^{-4}$)	11.5	8.5	8.5	22
B ($x10^{-4}$)	6.3	10.7	8.0	8.4
C ($x10^{-4}$)	0.9	0.9	0.9	0.9
U_c ($x10^{-4}$)	5	5	5	5
L_c ($x10^{-4}$)	4	4	4	4

Results

The annual Cd balance can be expressed as the ratio of inputs over outputs (I/O). The integrated system (I/O=2.5) and the conventional system with organic fertilizer (I/O=3) have a lower I/O ratio than the ecological system (I/O=5.2) and the conventional system with mineral fertilizers only (I/O=7.4). This results from the relatively low level of Cd input via fertilizer applications (no use of triple superphosphate) and the cultivation of crops that have a high Cd uptake rate (carrots, sugar beets, ware potatoes and onions). The ecological system has a higher input/output ratio since 47% of the total surface is cultivated with cereal crops (limited Cd offtake) and the inputs via manure applications are significant as well. It has to be noticed (for a fair comparison) that this is partly due to high manure applications to raise the phosphorus status of the soil in the initial phase of the experiments.

The total soil content (G) is the sum of the fixed and the adsorbed amount of Cd. The fixed fraction of Cd cannot be released to the soil solution, and it is more realistic to exclude it from the balance calculations. De Wit (1989) estimated the fixed fraction for the Nagele soil to be 0.28 mg kg^{-1}. The 'corrected' total (*i.e.*, labile) soil content has been used to calculate the total soil content, leaching and plant uptake of the farming systems in the course of time.

In Table 9.2, the values for the (critical) soil contents, the (critical) sustainability factors and the (critical) sustainability times are presented for the four systems.

Table 9.2. Output parameters of four arable farming systems.

Results:	Ecological	Integrated	Conventional-OF	Conventional-MF
G_{ss} (mg kg^{-1})	1.31	0.80	0.94	1.74
G_u (mg kg^{-1})	0.82	0.60	0.71	0.69
G_s (mg kg^{-1})	1.72	1.72	1.72	1.72
F_d	1.28	0.94	0.94	2.44
F_e	4.00	1.67	2.13	4.73
F_u	2.29	1.60	1.53	3.57
F_s	0.01	0.13	0.21	1.03
t_e	145	306	245	70
t_u	622	362	696	153
t_s	-	-	-	3366

Comparing the discrepancy factors (F_d) of these systems, already gives an idea about the most sustainable options. For the ecological and conventional-MF systems, the F_d-value is larger than 1 and for the integrated and conventional-OF systems it is smaller than 1. Based on the discrepancy factor, most problems are expected for the conventional-MF system and no real problems are expected for the integrated and conventional-OF systems. The values of the sustainability factors are good indicators of the most threatened compartment at steady state. For all systems F_e>F_u>F_s and thus F_c equals F_e. This suggests that, at steady state, ecology is threatened most and groundwater least for current standards. According to the sustainability times all standards will be exceeded for the conventional-MF system, but the time span varies between 70 and more than 3000 years for ecology and groundwater, respectively.

Although the F_d-value is smaller than 1 for the integrated and conventional-OF systems, in both systems the F_u-value is larger than 1 and the crop quality standards will be exceeded. These results illustrate that for discrepancy factors close to unity the effect for the least threatened object (leaching in this case) may mask the violation of the standard for the other output term (here uptake). Thus, neither for the integrated nor for the conventional-OF system the discrepancy factor identifies the violation of crop quality standards. Moreover, the discrepancy factor does not identify any problems for ecology, while the F_e-values are largest in every system. Hence, even for F_d-values of order 1 it may be worthwhile to estimate the sustainability factors in addition to the discrepancy factor if the required information is available.

The solution of the balance equation for the four systems is summarized in Figures 9.1-9.3. The time scale of 250 years is chosen because it is relevant for the sustainability principle. In Fig. 9.1, the ratio of the total soil content over the ecological quality standard is shown in the course of time.

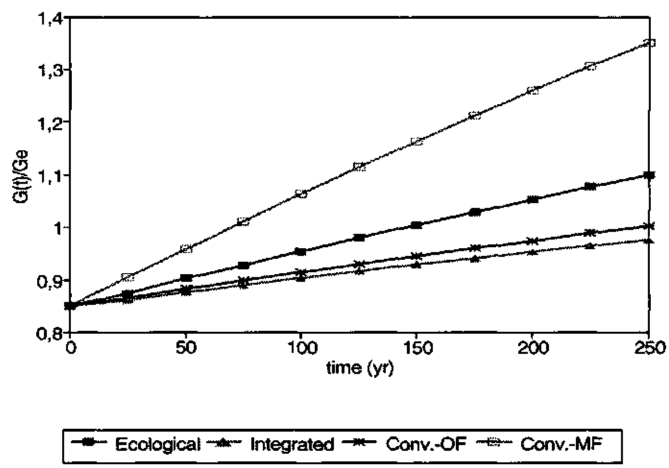

Figure 9.1. The ratio of the total soil content over the ecological quality standard of an ecological, an integrated, a conventional-OF (both mineral and organic fertilizer), and a conventional-MF (mineral fertilizer only) arable farming system in the course of time.

It is clear that the accumulation rate is the largest for the conventional-MF system followed by the ecological, conventional-OF, and integrated systems, respectively (Fig. 9.1). The integrated system has the lowest input rate and the highest value for the plant uptake rate parameter. This results in the highest t_e value. The ecological system has a relatively high input rate and has the lowest value for the plant uptake rate parameter. This results in the lowest t_e value after the conventional-MF system. Due to the high input in the conventional-MF system, it has the lowest value of all sustainability times.

The development of the crop uptake and leaching in the course of time is shown in Figs. 9.2 and 9.3, respectively.

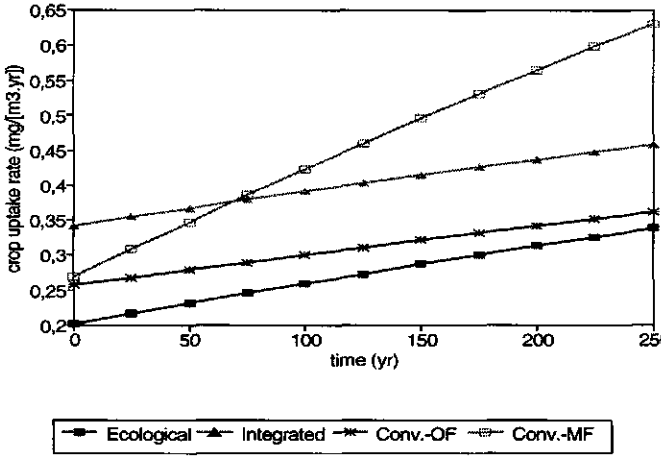

Figure 9.2. The crop uptake rate of an ecological, an integrated, a conventional-OF (both mineral and organic fertilizer), and a conventional-MF (mineral fertilizer only) arable farming system in the course of time.

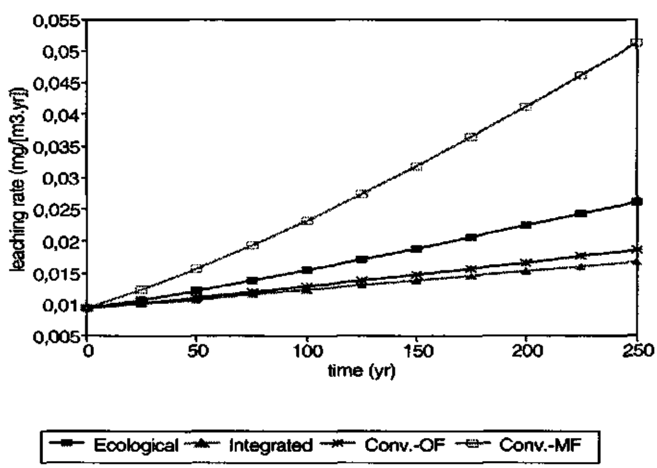

Figure 9.3. The leaching rate of an ecological, an integrated, a conventional-OF (both mineral and organic fertilizer), and a conventional-MF (mineral fertilizer only) arable farming system in the course of time.

Crop uptake in the integrated system starts at a relatively high level but is exceeded by the conventional-MF system after several decades due to the higher accumulation rate and the resulting higher total content in the latter system. Although the

values of the plant uptake rate parameters of the conventional-MF and conventional-OF systems are comparable, the resulting uptake rate in the conventional-MF system is much higher due to a higher accumulation rate and the resulting higher total content. The low value of the plant uptake rate parameter of the ecological system results in the lowest total uptake rate (Fig. 9.2).
In all farming systems, the F_s-value is lowest. This shows that no problems are expected with regard to solute leaching to the groundwater (Fig. 9.3).
The comparison of these four different arable agro-ecosystems shows that the selection of crops and fertilizers has a direct influence on the long-term development of the Cd concentrations in soil, groundwater and crops. The total Cd content at steady state exceeds the Dutch reference value in all four farming systems. Although the total Cd contents are rather high, the Cd concentrations in leachate stay below the critical level for all farming systems (except marginal exceedance for the conventional-MF system) due to the high adsorption capacity of this particular soil.

Discussion and conclusion

Current standards are not directly related to other compartment's standards. Our approach, though still limited, elucidates the importance of functional relationships involved for soil and other threatened objects and the need to relate standards.
Figs. 9.1-9.3 show the kinetics and magnitudes of the changes. These agree with the calculated values of the sustainability factors and times. It was shown that the most threatened object at steady state depends on which sustainability factor is critical. Strong non-linearity (n=1/2) did not change the sequence of the sustainability times in relation with the ranking of the discrepancy factors.
The sustainability indices should still be considered indicative at the moment, as the relevant soil, crop and other data are only approximately known at field or farm level. However, they suffice for screening and comparing different agro-ecosystems without having to know all processes in detail and thus allow for an assessment on a relative basis. Such an assessment may reveal:
1) which heavy metal may cause the largest violation of standards;
2) which environmental compartment is threatened most and for which compartment problems may be expected first;
3) which experimental data assessment should have priority in view of decreasing uncertainty and optimizing predictions;
4) which approaches to avoid violation of standards are feasible and most effective.

The study of specific agro-ecosystems on specific soils (as is done in the case studies) is very interesting. Another field of application may be the incorporation of sustainability indices in a generic data set like a Geographical Information System (GIS). If the parameters in a GIS could be combined in such a way that the rate parameters (A, B and C) were known, this could be very promising for larger scale (*e.g.*, whole region) assessments.

The proposed approach is not only valid for toxic or non-essential elements like Cd. Also essential elements, like Cu and Zn, with a nutritional function and potential deficiency problems for crop production may be taken into account. Both depletion and accumulation are related to sustainable agricultural practices and hence to the sustainability indices. However, for essential elements, appropriate standards for crop and groundwater quality may not always be defined. Moreover, depletion means by definition that the input rate is smaller than the output rates and the meaning of the sustainability indices should be evaluated carefully in that case. For example, in Eq. 9.11, this changes the signs (like: $[(B+C)G_0 - A]$) and thus the largest sustainability factor is exceeded last in that case.

In terms of environmental management, it is important to discriminate between processes that can and that cannot be easily managed. Quality standards are based on policy choices. The crop production rate and the groundwater recharge rate are only partly influenced by human management (within economic constraints) and mainly determined by natural factors like soil type and climate. In the same way, the input rate is mainly determined by human influences, but can only be partially reduced by agriculture. The values of plant uptake and leaching rates mainly depend on natural processes, but may be influenced as well.

By definition, the steady state is reached when the accumulation rate becomes zero. As the steady state depends on the input and output rates, it may be 'forced' at a designated level of G. Different strategies for cadmium management will have different consequences for the resulting steady state. Short-term strategies may aim at increasing the soil's buffer capacity. Sorption parameter k_f (and to a lesser extent also n) varies with soil type and pH. For soils with a low sorption (or buffering) capacity, the value of k_f is low. In that case, Cd concentrations are expected to increase in groundwater and crops. This may result in exceedance of groundwater and crop quality standards and at the same time in little accumulation.

'Good management practices' might attempt to lower the crop uptake rate (B) *e.g.*, by raising the organic matter content (increasing retention), favoring competition by applying calcium and magnesium and heavy metals like Zn, preventing irrigation with saline waters because higher chloride concentrations lead to higher Cd uptake, changing tillage practices to influence the stratification of pH, organic matter and Cd content, changing cultivar, and liming acid soils to increase the pH (Oliver *et al.*, 1993, 1994; McLaughlin *et al.*, 1994, 1995). Some practices that aim at lowering crop uptake (like stimulating competition) may at the same time lead to higher leaching rates or vice versa, thus resulting in a trade-off between leaching and uptake. Moreover, minimizing output levels by management practices will result in the steady-state content being reached later at a higher level. Selecting cultivated crops with pronounced Cd removal (within critical limits) can be very sensible for farming systems with low input. A higher uptake rate results in a lower steady state content, less accumulation, higher crop offtake and F_u, and a lower value of G_u.

Long-term strategies focus on reducing inputs to soils. This results in the steady state being reached with lower total accumulation and lower output rates, as was shown for the integrated system. Input reduction can be reached by reducing the amount of heavy metals in source material (quality) and by reducing the amount of fertilizer or manure added to the soil (quantity). This kind of input reduction could be aimed at by legislation, economic instruments, technology (*e.g.*, Cd removal from fertilizer raw materials), decreasing application rates and levels for maximum phosphate (P) addition, and by educating farmers on how to use nutrient and heavy-metal balances.

In our case study, the conventional-MF system with the use of mineral P-fertilizer shows the worst results. Mineral P-fertilizers like triple superphosphate can have a very high Cd content resulting in high contents of potentially bioavailable soil Cd. This could lead to the conclusion that mineral P-fertilizers should be either avoided or qualitatively improved in terms of their Cd/P_2O_5 ratio. Alternative sources of P are organic fertilizers like manures or composts. Because there is no fixed ratio between Cd and P in manures, determination of the Cd/P_2O_5 ratio is necessary before the selection of the most appropiate manure takes place. In judging these different types of fertilizers one should be careful to take into account all relevant aspects which are related to the use of these fertilizers. In the case of Cd it can be argued that because input by fertilizers is by definition diffuse and accounts for a substantial percentage of the soil input, mineral fertilizers should be produced Cd free. However, concluding that it is unacceptable to continue the application of Cd-rich fertilizers and enforcing standards or economic instruments to shift towards the use of low-Cd ores, necessitates the development of processes that remove Cd from P-ores during fertilizer production (Vonkeman, 1996). Measures have to be justified in terms of legitimate environmental, human health, industrial and trade policy objectives. Moreover, a drop in Cd flows to soils in one country should not lead to problem shifting by increasing the flow to agricultural soils in other countries.

In this chapter, we have provided a tool for objective decision making as far as 'heavy metals' are concerned. Clearly, suggestions to improve the heavy-metal balances of agro-ecosystems are motivated by environmental concerns. Sustainability in a wider sense of agricultural production encompasses other than environmental factors. The only ideal approach to achieving 'sustainable heavy-metal management' has to be integrated and consistent. It involves good Zn, P, manure, and trade policies on the national and international level as well: there are no cheap solutions.

The sustainability indices meet some important criteria that have been identified by Gilbert and Feenstra (1994); they are representative for the chosen system, scientifically founded, quantifiable and representing the cause-effect chain for agricultural soils. Moreover, they indicate some points of action for heavy-metal policy and management, like setting up monitoring programs to determine the rate of input, output and accumulation regarding agricultural soils. In this way, regional strategies for heavy-metal management could be developed.

CHAPTER 10

REQUIREMENTS FOR CALCULATING DYNAMIC HEAVY-METAL BALANCES OF SOIL

Abstract

In this chapter, literature is reviewed with regard to heavy-metal balances in long-term field experiments. Effects of heavy-metal accumulation on uptake by plants were studied with soil from a long-term field trial involving different organic amendments. Dynamic heavy-metal balances are useful for projective purposes. Further development of dynamic modeling would be made possible if requirements are met that enable quantification of probability distribution functions of input and output rate parameters. The data needed could be gathered by setting up research and monitoring programs with regard to the fate of heavy metals in agro-ecosystems and other (economic) sectors of our society.

Introduction

Recycling of biosolids by agricultural utilization allows the exploitation of raw materials which otherwise would be incinerated or dumped. Land application of wastes may fulfil several objectives like reducing the problem of waste disposal, conserving water and nutrient resources and preventing soil degradation and erosion (Cameron *et al.*, 1997). The question is whether the soil-crop system can be used to assimilate waste components in a way that does not adversely affect the quality of soil and other environmental compartments.

The fate of the heavy metals Cd, Cu, Pb, and Zn in agro-ecosystems is of concern because they are toxic to plants, animals and man. The control of heavy-metal fluxes is therefore one of the prerequisites for sustainable agricultural production. Agricultural cycles (soil - fodder - livestock - manure - soil, and soil - food - human wastes - soil) are contaminated by heavy-metal inputs that may occur anywhere in the cycle, *e.g.*, in the urban environment (corrosion, etc.), during transport processes, and by supplementing feed. The use of waste products as soil conditioners and/or fertilizers thus may cause ever increasing heavy-metal flows (back) to agricultural soils on top of fresh inputs from mineral fertilizers, manure, atmospheric deposition, etc. Accumulation of heavy metals in agricultural soil may thus occur as a side effect of measures aimed at closing cycles. Heavy-metal balance sheets may be used as sustainability indicators in a generic approach (Chapter 2). If accumulation occurs, the system is 'off balance'. Of course, different spatial scales are involved. Farm-gate balances can be used as on-farm management instrument and balances on the field-scale enable a direct link with criteria for soil protection and other environmental compartments (Chapter 4). In that respect, it is also clear that accumulation of heavy metals in soil (plough layer) should not be the only point of focus. Insight is needed in future developments of heavy-metal fate to be able to judge the long-term consequenses of certain practices. A predictive model for the long-term behavior of heavy metals in agricultural soils requires information about long-term trends in heavy-metal inputs from different sources, about changes in soil, crop and climatic conditions and about the behavior of heavy metals in soil-crop systems under different conditions. Because this information is not available, another approach towards modeling future developments is needed. Projection may be fruitful because it shows the possible patterns of behavior represented in the dynamic relations among variables, it enables the calculation of possible future development paths, and it helps to identify data needed to fill in gaps in current knowledge (Rykiel, 1984). Long-term experiments may serve to validate projective models.

In this chapter, measurements at a long-term experimental field trial involving different organic amendments are interpreted with regard to the question how soil composition and heavy-metal contents have been affected. Also, literature is reviewed with regard to heavy-metal balances in long-term field experiments. Based on these different studies, data requirements for projective purposes are discussed.

Materials and methods

The organic amendments trial at the "Van Bemmelenhoeve"

Organic matter plays an important role in retaining heavy metals in soil and therefore it is interesting to study the changes in soil composition, heavy-metal content, and heavy-metal adsorption capacity as affected by different organic amendments applied for a long time. On the Prof. dr. J.M. van Bemmelenhoeve (105 ha) in the Wieringermeerpolder (the Netherlands, 52° 48′ N; 5° 3′ E), such a long-term experiment was initiated in 1933. Before the reclamation in 1930 the polder was part of the Zuiderzee. In 1945 (during the second World War) it was flooded again by the sea for a short time.

On arable land, different treatments (cf. Table 10.1) were applied and their effects on crop yield, organic matter development, and N supply studied. The lay-out of the experiment did not include any replications.

Table 10.1. The experimental fields of the Van Bemmelenhoeve.

Field	Year started	Amount applied or frequency
Mineral fertilizer (MF)	1933	only crop residues (straw removed)
Farm yard manure (FYM)	1937	40 ton every two years
Green manure (GM)	1937	every two years
Compost (CO)	1948	40 ton every two or three years
Straw (S)	1948	about every three years (grain residues)

The objective of our study was to determine the extent of changes, if any, resulting from the long-term use of animal manure, catch crops, town refuse compost, straw and mineral fertilizers on this soil. More specifically, we wanted to know the effect of these treatments on:

- top-soil composition (organic matter content and texture);
- heavy-metal accumulation and vertical stratification;
- heavy-metal content in crops;
- adsorption and fixation of (added) metals.

On the compost field, town refuse compost (so-called VAM-compost) had been used since 1948. The total amount of this compost applied is about 720 ton (18 x 40 ton). In 1991 and 1994, 40 ton source separated organics (SSO-) compost was applied. The exact composition of the soil amendments is unknown, but Table 10.2 gives an impression. The heavy-metal contents in SSO-compost are based on analyses in 1993 (Brethouwer, pers. comm.) and are applicable to the additions in 1991 and 1994. The heavy-metal contents of VAM-compost were also supplied by Brethouwer.

Table 10.2. Composition of composts.

	VAM-compost		SSO-compost
	before 1966	1966-1983	
% dry matter	65	65	70
% organic matter[1]	18	18	30
Cd (mg kg^{-1})	7.3	12	0.74
Cu (mg kg^{-1})	512	870	33
Pb (mg kg^{-1})	850	1300	82
Zn (mg kg^{-1})	1640	2500	160
Zn/Cd (-)	225	208	216

1. expressed on dry weight

Before 1967, household coal was commonly used as fuel. As a result, "organic matter" in town refuse compost consisted for ca. 60% of non-combusted remnants of household coal. This changed after the introduction of natural gas as a main source of energy (De Haan, 1981a).

Soil sampling and analysis

The size of the five experimental fields is 11x240 meters. Soil was sampled in May, 1995. The edges (2 meters between the fields and 30 meters at the ends) were not sampled. Mixed samples consisting of 16 cores were taken per field to enable comparisons between the fields. Samples were taken at depths of 0-0.2 m, 0.2-0.3 m, 0.3-0.4 m, and 0.4-0.6 m below surface. Also, a mixed sample (4 sub-samples) of the plough layer (0-0.3 m) was taken. This sample was used in a pot experiment with Swiss chard (as described in the part on 'bio-assay'). From every mixed sample two sub-samples were taken for further analysis. Analyses were done in duplicate for both samples.

We determined (pseudo) total Cd, Cu, Pb and Zn contents in the soil samples after digestion with *Aqua regia* or extraction with 3 M HCl in a boiling waterbath. Results obtained with these methods are similar for Cd and Pb but the HCl extraction has a lower detection limit.

Soil pH was determined in 1 M KCl. Carbonate content was determined by dissolving carbonates with HCl (Scheibler method). The percentage organic carbon was determined by dichromate ($K_2Cr_2O_7$) oxidation in which the concentration of Cr^{3+} ions is measured spectrophotometrically. CEC was measured using unbuffered 0.01 M $BaCl_2$ and texture was determined using pipette and sieve. All measurements were carried out in duplicate. For details on the analytical methods we refer to Houba *et al.* (1995).

Plant sampling and analysis

Plant uptake in the field was measured by taking potato (*Solanum tuberosum* L. var. Agria) samples. In July (at maximum soil coverage by leaves), we sampled the leaves and in September we gathered the tubers (both: composite samples of 10 plants per field). Heavy-metal contents were measured after microwave digestion (in duplicate) according to the provisional procedure provided by the laboratory of Soil Science and Plant Nutrition (Novozamsky *et al.*, 1996).

Bio-assay

A factorial pot experiment was designed (2.5 kg soil per pot + nutrient [N, P, K, Mg, B, Mn, Mo] solutions) in which different levels (n0-n1-n2-n3) of Cd, Cu, Pb and Zn were established by adding metal-salt (nitrate) solutions in a ratio 1: 10: 20: 80 Cd to Cu to Pb to Zn. This ratio roughly corresponds to the mean ratio of these four metals in atmospheric deposition. Each treatment was done in triplicate for each of the 5 fields (12 pots per field).

Beta vulgaris L. sp. vulgaris var. Cicla (Swiss chard) was used as test crop to answer the question 'to what extent are the (added) heavy metals adsorbed to the soil and to what extent are they taken up by the crop'. After 3 weeks of incubation with the heavy-metal solutions, Swiss chard was sown. Two weeks thereafter the number of plants was reduced to 5 per pot. The plants were harvested after 6 weeks and heavy-metal contents were determined after microwave-digestion.

Results

In this section, we first describe effects of the different treatments on soil composition and then effects on soil functions (*i.e.*, plant uptake and sorption capacity).

Soil composition

In Tables 10.3-10.6, an overview of the effects of the different treatments on soil composition is given. Organic matter contents (Table 10.3) were calculated by multiplying the organic carbon content by 1.73, thus assuming that about 58% of the organic matter consists of organic carbon.

Table 10.3. Soil organic matter contents (%) of the experimental fields.

	Mineral	Animal manure	Green manure	Compost	Straw
0-20	1.9	2.4	2.1	2.9	2.0
20-30	1.9	2.3	2.1	2.9	2.2
30-40	1.9	2.4	2.1	2.8	2.0
40-60	2.0	2.0	2.4	2.0	1.9

The fields on which organic amendments have been applied have similar organic matter contents except for a higher organic matter content in the soil of the compost field. The mineral field has the lowest organic matter contents.

The texture of the plough layer is given in Table 10.4.

Table 10.4. Soil texture of the experimental fields: percentage expressed on mineral constituents of fine earth (*i.e.*, constituents <2 mm and expressed in μm).

	Mineral	Animal manure	Green manure	Compost	Straw
<2	20.9	21.9	19.8	19.6	20.8
<16	30.1	32.1	30.8	29.2	30.9
2-50	21.3	19.6	18.0	17.1	19.5
>50	57.6	58.3	62.5	63.2	59.6
>2 mm	1.3	1.2	2.8	3.5	1.3

Based on these results the soil can be classified as a sandy clay loam. Particles > 2 mm mainly consisted of shell-pieces. In the soil of the compost field not only shell-pieces but also lots of glass pieces and black beads (*i.e.*, household coal) were found. The farm yard manure field has the largest largest clay fraction while the compost field has the smallest clay and silt fraction and the largest sand fraction. The textural changes in the soil induced by the organic amendments appear to be small. The heavy-metal contents at several depths are shown in Table 10.5.

Table 10.5. Heavy-metal contents at several depths (mg kg^{-1}) of the experimental fields.

	Cd-HCl	Cu-AR	Pb-HCl	Zn-AR	Zn/Cd
Depth (cm):	Mineral fertilizer:				
0-20	0.30	26.5	13.7	45.6	152
20-30	0.35	28.3	13.6	45.0	
30-40	0.30	26.5	14.3	48.2	
40-60	0.21	18.0	11.8	43.8	
	Farm yard manure:				
0-20	0.31	30.5	15.6	51.9	167
20-30	0.33	32.3	16.1	68.8	
30-40	0.33	33.0	15.3	57.5	
40-60	0.21	22.3	12.8	52.5	
	Green manure:				
0-20	0.35	35.1	24.8	72.8	208
20-30	0.37	35.0	26.7	76.3	
30-40	0.35	35.0	28.2	76.3	
40-60	0.21	18.0	17.9	52.5	
	Compost:				
0-20	0.74	74.0	117.8	218	295
20-30	0.67	67.0	87.2	193	
30-40	0.74	72.0	78.0	195	
40-60	0.28	30.8	40.0	103	
	Straw:				
0-20	0.28	21.4	12.9	45.0	161
20-30	0.38	19.0	13.4	40.0	
30-40	0.26	23.3	12.0	51.3	
40-60	0.14	9.5	9.7	47.5	

Cadmium and Pb were extracted with HCl and Cu and Zn with *Aqua regia*. The fields with organic amendments (except for straw) show increased heavy-metal contents in the soil compared with the mineral field. The compost field and the mineral field have the highest and the lowest heavy-metal contents, respectively.
The results for $CaCO_3$, organic matter (OM) clay, and the CEC of the plough layer (0-0.3 m) are given in Table 10.6.

Table 10.6. Some characteristics of the soils used in the bio-assay.

	OM (%)	Clay (%)	$CaCO_3$ (%)	CEC (cmol$^+$ kg^{-1})
Mineral	2.0	17.5	11.5	12.6
Manure	2.6	18.5	11.7	13.6
Catch crop	2.2	17.0	10.7	12.9
Compost	2.8	16.5	10.4	13.5
Straw	1.9	18.0	10.5	12.6

The soil of the experimental fields is calcareous and the pH-KCl was about 7.6 for all soils.

Soil functions
The results for the potato analyses are shown in Table 10.7.

Table 10.7. Potato: heavy-metal contents in tubers and leaves (mg kg^{-1} DW) of the experimental fields.

	Mineral	Manure	Catch crop	Compost	Straw
Cd					
tuber	0.042	0.06	0.053	0.064	0.043
leaf	0.367	0.372	0.308	0.242	0.316
Cu					
tuber	4.5	4.5	5.3	5.6	4.6
leaf	6.4	7.4	7.7	10.3	6.3
Pb					
tuber	0.47	0.36	0.42	0.36	0.23
leaf	2.9	1.5	1.7	3.1	1.1
Zn					
tuber	10.9	11.8	13.1	14.6	10.4
leaf	18.8	22.6	34.1	60.6	20.8

With regard to the compost field, it can be noticed that the contents in the potato leaves are lower for Cd and higher for Zn compared with the other fields that received organic amendments. Furthermore, metal contents in the leaves are higher than in the tubers (mainly so for Cd and Pb).

The added amounts of Cd, Cu, Pb, and Zn (mg kg^{-1}) for the Swiss chard bio-assay are given in Table 10.8.

Table 10.8. Added amounts of Cd, Cu, Pb, and Zn in the bio-assay (mg kg^{-1} dry soil).

	n1	n2	n3
Cd	1.5	3	4.5
Cu	15	30	45
Pb	30	60	90
Zn	120	240	360

Interpretation

Analysis of variance was used for the statistical analysis of the bio-assay results and 'significant' in this section means $p < 0.01$. The outcomes are interpreted and compared with findings in literature.

Pb:

The risk of food chain contamination posed by Pb in agricultural fertilizers is low since Pb is one of the least mobile heavy metal in soils. Moreover, plant-absorbed Pb concentrates in the roots (McBride, 1994) since movement of Pb into higher plants is impeded by a number of biochemical and/or physical processes involving Pb binding, inactivation and/or precipitation. Health concern with Pb in soils arises mostly from the contamination of plants by soil particles, and ingestion of soil by humans and grazing animals. Plants may thus merely act as passive Pb carriers in the food chain. Gerritse *et al.* (1983) could not find any significant relationship between plant uptake and soil solution concentration or any other soil parameter for Pb. Gerritse & Van Driel (1984) measured distribution constants for 33 temperate soils. Extractable concentrations were found to lie in a range of about 1 to 5% of total metal in the soils for Pb and ca. 10 to 50% for Cd, Zn and Cu. Lead in soils was thus less accessible than Cd, Cu and Zn. Sloan *et al.* (1997) found that lettuce tissue contents of Cd, Zn and Cu were significantly correlated with total heavy-metal contents in the soil. Lead uptake was unaffected by multiple biosolids applications. After 15 years of biosolids applications, the relative bioavailability of heavy metals applied with biosolids was Cd >> Zn > Cu >> Pb. Results of their study show that significant amounts of biosolids-derived Pb can be applied to soil with no long-term increase in easily extracted forms of soil Pb.

Analysis of the bio-assay results shows no differences between the fields if no metals are added. Adding Pb to the soil did not result in any increased uptake and did not result in any differences between the fields either. Clearly, Pb is very strongly adsorbed and there was no additional uptake in the pot experiment.

In the case of Pb, atmospheric deposition and soil adhering to crops are expected to play a more important role than Pb uptake from the soil. Dalenberg & Van Driel (1990) found that atmospheric deposition contributed considerably (73-95%) to the Pb contents in the leafy material of grass, spinach and carrot. Van Straalen & Bergema (1995) studied the influence of changing bioavailability on the ecological risk of Cd and Pb in soil and found that a non-linear increase of the ecological risk may occur due to both speciation changes of the metal (non-linearity between bioavailability and pH) and the curvature of the inter-species sensitivity distribution (non-linearity between bioavailability and ecological risk). Their example shows that regarding future ecological risks of the presence of Pb, soil pH is very important. However, this calcareous soil is not sensitive to acidification at all.

Cu:

Jarvis (1981) stated that over a wide range of total contents in a range of soils there is little relationship between Cu contents in soils and those in plants. Van Luit & Henkens (1967) found that there was no further increase in the Cu content of perennial rye grass, red clover and herbage after a Cu level of 5 mg kg^{-1} ($Cu-HNO_3$) was reached in different humic sandy soils.

The bio-assay results without added metals show that the Cu contents in plants grown on the soil of the mineral field are lower as compared to the organic fields. This might be the result of Cu-DOC complexes that increase the transport of Cu to the roots in the case of the organic fields. The contents in plants grown on the compost field soil are not significantly higher than in plants grown on soil of the other organic fields. After adding metals to the soil, there is a clear increase of Cu contents in Swiss chard on all soils except the green manure soil with the largest effect for the smallest addition. At higher additions, the increase is generally steady but low while the difference between the mineral field and the organic fields disappears (Fig. 10.1).

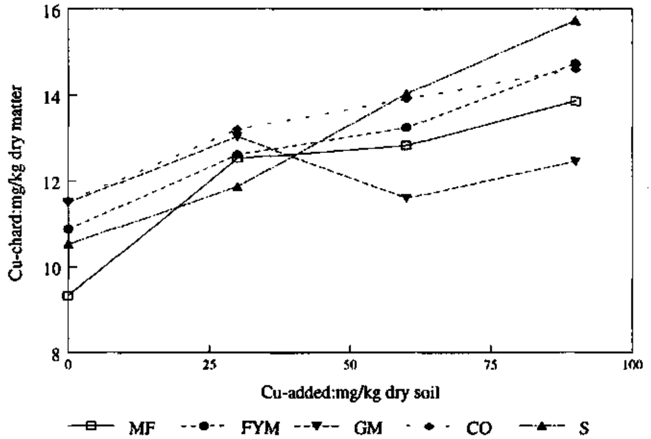

Figure 10.1. Relationship between Cu additions to the soils of the experimental fields and Cu uptake by Swiss chard (MF: mineral fertilizer; FYM: farm yard manure; GM: green manure; CO: compost; S: straw).

Cd and Zn:

The combination of a generally high bioavailability in soils and very high toxicity to animals and humans causes Cd to be the element of greatest concern in considering the value of soil amendments.

The bio-assay shows higher Cd uptake from the soil of the mineral field as compared to the organic fields. Thus, on the mineral field, Cd uptake is higher despite lower soil contents. The compost field has (by far) the highest Cd contents (Table 10.5). However, Cd uptake from on the compost soil is not significantly higher than uptake from the other organic fields. After addition of metals to the soil, there is a clear (linear) increase of Cd content in Swiss chard related to the amount of Cd added. This increase does not differ significantly for the soils of the different experimental fields (Fig. 10.2). The difference between uptake from the soil of the mineral field on the one hand and the uptake from the soils of the organic fields remains.

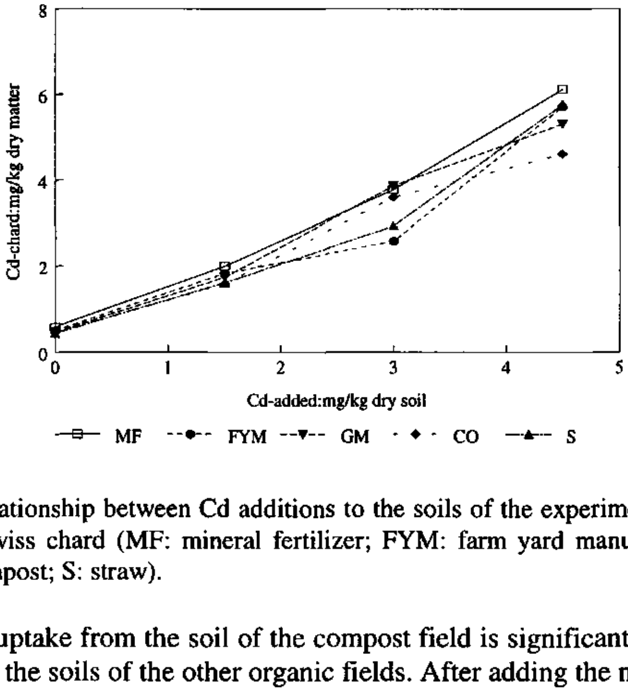

Figure 10.2. Relationship between Cd additions to the soils of the experimental fields and Cd uptake by Swiss chard (MF: mineral fertilizer; FYM: farm yard manure; GM: green manure; CO: compost; S: straw).

Regarding Zn, uptake from the soil of the compost field is significantly higher than the uptake from the soils of the other organic fields. After adding the metals, there is a clear increase of Zn content in Swiss chard related to the amount of Zn added. This increase is less profound on the compost soil and the difference between the compost soil and the other (organic) soils disappears at higher amounts added (Figure 10.3).

Zinc and Cd may compete for binding sites in the soil system and for uptake sites in the plant. Due to the varying mechanisms in which Cd and Zn may interact, the ultimate effect of Zn additions on a soil-crop system varies depending on relative Cd and Zn concentrations, soil properties, and plant characteristics (Grant & Bailey, 1997). According to Tiller (1989), interaction of Cd with Zn can be positive, negative, or nonexistent, depending on the relative concentration levels, the soil and the crop. Gerritse *et al.* (1983) in a pot experiment with vegetables on 20 Dutch soils found that increasing Zn appeared to increase Cd uptake at high solution concentrations of Cd and to decrease uptake at low solution concentrations. Oliver *et al.* (1994) found that treating Zn deficiency with small amounts of Zn fertilizer (up to 5.0 kg Zn ha^{-1}) significantly reduced wheat grain Cd contents.

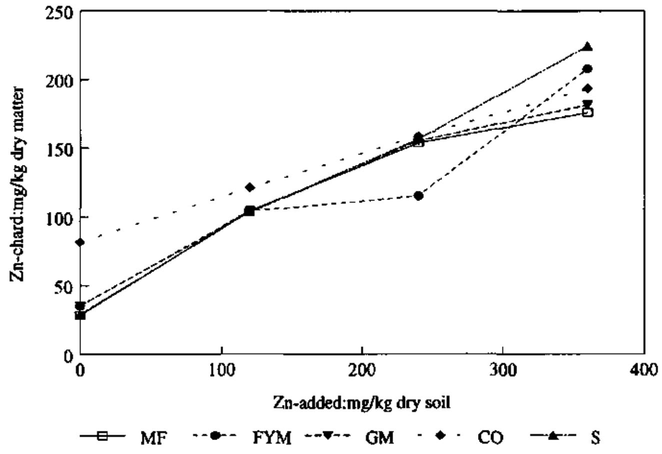

Figure 10.3. Relationship between Zn additions to the soils of the experimental fields and Zn uptake by Swiss chard (MF: mineral fertilizer; FYM: farm yard manure; GM: green manure; CO: compost; S: straw).

Oliver et *al.* (1994) suggest that in areas where high Cd concentrations in grain are of concern, Zn should be applied to soils suspected of being Zn deficient in order to safeguard grain quality. McLaughlin *et al.* (1995) found a significant reduction in potato tuber Cd contents with additions of Zn at planting (up to 100 kg Zn ha^{-1}) on soils not deficient in Zn at four of the five sites studied. However, factors associated with irrigation water quality at the sites (particularly the chloride concentration) appeared to dominate any effects of changing fertilizer type or Cd concentration. Phosphorus and Zn may also interact in their effects on Cd accumulation in crops. Grant & Bailey (1997) found that content and accumulation (defined as content times yield) of Cd in flaxseed were influenced by effects of Zn and P. Application of P (monoammoniumphosphate) increased both Cd content and accumulation and decreased Zn content in flaxseed. Application of Zn (zinc sulphate) generally decreased Cd content, but had little effect on Cd accumulation in flaxseed. Contents of Cd in flaxseed decreased as seed content of Zn increased and so lower Zn contents in the plant may lead to increased Cd contents in flaxseed (Grant & Bailey, 1997).

Novozamsky *et al.* (1993) showed the possibility of evaluating Cd/Zn interaction during plant uptake by measuring Cd and Zn in the same 0.01 M $CaCl_2$-extract and they found that (pH and) Zn strongly influenced the uptake of Cd from the soils and especially in a calcareous soil (comparable with the 'Bemmelen-soil') this effect was very strong.

In the case of the Bemmelen soil, we found high soil Cd and Zn contents as a result of compost applications. At the same time, the contents in potato (leaves) and Swiss chard were relatively high for Zn and low for Cd. Thus, the compost field shows low Cd uptake despite the highest Cd soil contents. Zinc contents are high in both soil and crop. Thus, Cd/Zn interaction on this soil is very likely. The initially very high Zn/Cd ratio in the compost soil shows that this ratio in soil has been increased by the compost applications (cf. Table 10.5).

Figure 10.4 shows that the Zn/Cd ratio in Swiss chard is much higher for the compost soil if no metals are added. After metal additions, the Zn/Cd ratio decreases due to the lower Zn/Cd ratio in the mixture of metal salts.

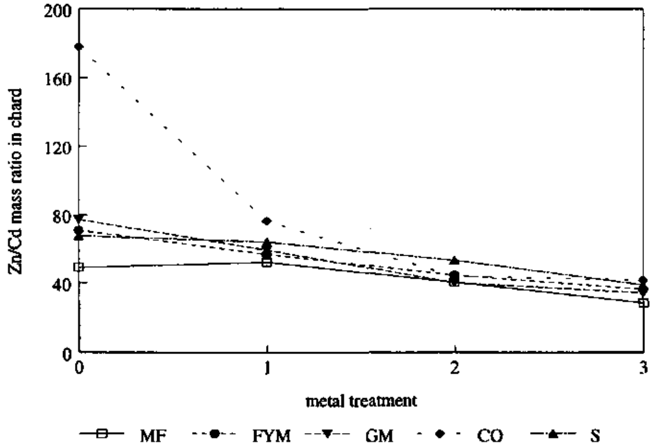

Figure 10.4. The effect of different metal additions to the soils of the experimental fields on the Zn/Cd mass ratio in Swiss chard MF: mineral fertilizer; FYM: farm yard manure; GM: green manure; CO: compost; S: straw).

Regarding food-chain risks, it has been suggested that Cd accumulation in the kidneys may depend on the Cd/Zn ratio since Zn may provide protection against excessive dietary Cd. In that respect, the Cd/Zn ratio of soil amendments would be important.

General discussion

The soil-crop system is dynamic in space and time and thus subject to short-term fluctuations and at the same time undergoing (gradual) long-term alterations in response to management and environmental factors. Changes in soil properties affect the form and availability of metals and need to be considered in the management of contaminated soils or the use of soils for disposal of waste materials (Alloway, 1990). In order to judge the long-term effects of these changes, two approaches need to be followed supplementary. One is the use of model predictions and scenarios and the other is the use of factual experimental data.

Scenario calculations

Deriving standards for soil quality, which are ecotoxicologically and agronomically sound is very complicated. McGrath *et al.* (1994) showed that differences in the philosophy behind environmental protection and in the choices of which organisms to protect, explain the different metal limits for sewage sludge which have been adopted in various countries. Total contents are not suitable to characterize soil quality because they are not directly related to soil functioning and effects. However, appropriate standards are difficult to formulate because (spatially and temporarily) variable soil parameters, like pH, should be taken into account.

The so-called 'crititical load approach' heavily depends on the choice of reliable soil quality standards that are related to adverse effects. The selected soil quality standard is used to derive the critical (or 'maximum acceptable') heavy-metal load. Comparing the critical load with the actual load shows how much input reduction is needed (De Vries & Bakker, 1996). According to this effect-oriented approach, soil quality standards would have to be coupled to air quality standards in order to minimize heavy-metal input by atmospheric deposition. In turn, these deposition standards would have to be translated in emission standards. If this approach were feasible at all, it would still lead to filling up the selected soil quality standard.

Although the Dutch environmental policy supports the effect-oriented approach in the Dutch soil protection law, the path to soil quality standards that are closely related to effects will be long and tortuous. Therefore, a source-oriented policy is needed to limit heavy-metal fluxes that are known to be too large. The use of heavy-metal balance sheets as an extension of existing standards enables a principally different way of guarding soil quality. Instead of the (desired) *status* of the soil, the central focus point for analysis is the *burdening* of the soil with potential toxic elements per unit time and area (flux) and the subsequent net accumulation in the soil system. For essential elements, input should equal output (at an optimum level of supply). For non-essential elements, the input should be smaller than or at the most equal to the permissible output (*i.e.*, output that does not exceed quality standards for ecosystems, crop and groundwater). Thus, the balance or flux approach requires an integrated evaluation of all heavy-metal inputs and resulting outputs (Furrer, 1984; Ferdinandus *et al.*, 1989). A balance of heavy metals in soil relates the rates of accumulation, input and output. The change in total heavy-metal content in soil depends on the input rate at the soil surface, the leaching rate at the lower boundary of the system and the removal rate by harvesting plants. Leaching and crop uptake of heavy metals are related to the metal concentration in the soil solution which depends on the labile heavy-metal content in soil and on sorption characteristics. The output rate coefficients depend on many chemical, physical, and biological properties. With projective dynamic balance calculations for the plough layer it is, in principle, possible to determine whether or not problems are likely to occur and, if so, in which compartment (soil, produce or groundwater) and on which time-scale (Moolenaar *et al.*, 1997a).

Long-term experiments

Interest in improving soil management practices has focused on low input, sustainable agriculture including the addition of animal manure, compost, sewage sludge and crop residues. Differences between matrices of heavy-metal carriers (*e.g.*, mineral fertilizer, manure, compost) cause the same heavy-metal loads to result in different accumulation patterns due to changes in soil composition and sorption capacity. Thus, fertilizer matrices may significantly influence soil properties and hence the buffering capacity of the soil. Metals may be present in organic fertilizers in various forms, including free ions, carbonates and both soluble and insoluble organic chelates. These forms affect their chemical reactions in soil (Mortvedt, 1996) and few are initially mobile in soil (Stover *et al.*, 1976).

In this respect, the soil organic matter (SOM) content may be of great importance within one type of soil. The amount of dissolved organic carbon (DOC) is related to the SOM content. Soluble organics may act as 'metal carriers', thus showing the importance of soluble organically complexed forms of metals in controlling availability for plant uptake (Minnich *et al.*, 1987). In contrast to Cu and Zn, it would appear that organic ligands do not have great significance in the complexation of 'free' Cd^{2+} in soil solution. However, evidence is emerging that in the vicinity of plant roots where organic anion concentrations may be high due to microbial activity or active excretion of organic ligands by plant roots, a significant proportion of the total Cd in solution may exist as organo-complexes (McLaughlin *et al.*, 1996). Sloan *et al.* (1997) suggested that high DOC concentrations in soils receiving large biosolids amendments initially inhibit Cd precipitation, but as biosolid applied organic matter stabilize and DOC concentrations decrease, subsequent Cd precipitation decrease Cd bioavailability.

Different cropping systems produce various types and amounts of residues which in turn may also influence the soil properties. Basta & Tabatabai (1992a) studied the effect of long-term cropping systems on heavy-metal adsorption. They found that cropping systems significantly affected soil properties (organic matter content, pH, CEC) and that single-metal adsorption-release behavior was affected by cropping systems due these changing soil properties. The extent to which soil properties changed was related to the buffering capacity of the soil, type and duration of the cropping system and to management practices that lead to altering pH and base saturation (Basta and Tabatabai, 1992a). They also investigated the effect of pH on heavy-metal adsorption by soils under different cropping systems and found that differences in metal adsorption depended on the initial heavy-metal content. At low contents, all the added metals were adsorbed regardless of the solution pH. At high contents, metal adsorption by soils increased with increasing solution pH (Basta and Tabatabai, 1992b).

Smilde & Van Luit (1983) compared trends in soil Cd in P treated and control plots in 18 long-term field experiments in the Netherlands. The overall trend was that soil Cd accumulated in the P-treated plots (0.002-0.01 mg kg^{-1} per year at a phosphate rate of 200 kg P_2O_5). A Cd dose estimated at 135-450 g ha^{-1}, applied over the years in five long-term field experiments, did not significantly increase Cd concentrations of wheat (grain), barley (grain), potato (tuber), sugar beet (leaf) and onion (bulb) grown on various soil types. Mortvedt (1987) determined whether or not periodic applications of P-fertilizers resulted in measurable Cd accumulation in soils and in harvested crops using samples from nine long-term (>50 yr) soil fertility experiments in the USA. Although Cd appeared to be accumulating in the soil at a slow rate, the results of the plant analyses showed few significant increases in Cd concentrations of plant tissues (maize, wheat, soybean). Jeng & Singh (1995) measured Cd accumulation in soils and crops due to the use of phosphate fertilizer in a 70 year-old fertilizer experiment in Norway. The annual increase in total Cd content of fertilized plots varied from 0.04-0.12%. The long-term experiments at Rothamsted show that where Cd has been added in superphosphate since 1889 there is little or no additional Cd in the topsoil of arable soils of neutral pH and low in organic matter, but appreciable accumulation in acid grassland soils with a higher organic matter content (Johnston & Jones, 1995).

Andersson (1983) studied the influence of heavy-metal additions with composted municipal refuse, sewage sludge, manure and NPK-fertilizers on the concentration in soil and crops. Annual compost and sewage sludge applications gradually increased the heavy-metal soil content. The parallel addition of organic matter in the organic fertilizers lead to a decreased crop uptake of Cd and Cu despite increased Cd and Cu soil contents. Manure, like compost, decreased Cd uptake by 30% as compared to NPK-fertilizer. This was caused by the differences in pH and organic matter content resulting from the differences in fertilization. In comparison with NPK-fertilizers, the organic fertilizers also had a depressing influence on the uptake of Cu and Pb despite the soil Cu content being doubled at the highest applications of compost. Hence, soil amendments not only affect the heavy-metal soil content but also alter heavy-metal solubility and availability in a way that the solid/liquid phase equilibrium and the resulting heavy-metal accumulation are changed.

Plateau or time bomb?
There exist two hypotheses regarding absorption of potentially toxic metals by plants grown on sewage sludge-treated soils (McBride, 1995; Chang *et al.*, 1997). The 'sludge protection' hypothesis or 'plateau' theory poses that the soil's metal adsorption capacity added with sludge (largely due to organic matter) persists as long as the metals persist in the soil and that metals remain in chemical forms not readily available for plant uptake so that there will be an equilibrium between sludge- and soil-borne metals at which plant absorption approaches a plateau (*e.g.*, Chaney & Ryan, 1993). The 'sludge time bomb' hypothesis poses that although the metal adsorption capacity of the soil is augmented by soil organic matter, this adsorption capacity will revert back to its original level after terminating sludge application. Since the mineralization of organic matter releases adsorbed metals into more soluble forms there is the potential of a time bomb (McBride, 1995).
The essential question is what will happen to the toxic metals in the long run after the cessation of sludge applications. In order to answer this question one needs to know whether the added protective effect of the sludge residue arises from the organic (prone to decomposition) or from the inorganic materials (like phosphates, silicates, Fe-, Al- & Mn-oxides). The sludge protection hypothesis requires that the inorganic materials in the sludge adsorb or precipitate the toxic elements. Although it may not be possible, based on field experiments, to discern the relative importance of organic and inorganic constituents in sludge with respect to limiting heavy-metal availability, long-term research is needed to determine if the solubility or activity of these metals changes significantly as sludges further decompose in the soil (McBride, 1995).
Hooda & Alloway (1994) found for two sludge amended soils a trend towards increasing plant metal accumulation over successive harvests for several metals, which appeared to be caused by a progressive decline in pH and organic matter status. Hooda *et al.* (1997) found that plant availability of heavy metals differed widely among wheat, carrot and spinach on 13 sludge-amended soils which had equilibrated in the field for several years after sludge applications. This showed that metal uptake is plant-species dependent. Furthermore, accumulation of Cd and Zn in the plants showed greater increases than the Cu and Pb accumulation in the plants. Miner *et al.* (1997) studied the relationship between plant concentrations of Cd, Cu, and Zn and soil properties on sites of long-term municipal sludge applications. Best fit models for Cd and Zn in Swiss chard primarily depended on extractable metal concentration and soil pH. Zhao *et al.* (1997) reported investigations of soil-plant transfers of Cd and Zn in a long-term field experiment which started in 1942 at Woburn, UK. Chemical extractability and bioavailability of sludge-born Zn and Cd remained high in a neutral sandy loam during the 24 years after application of sewage sludge ceased (1961). Zn and Cd concentrations in carrot and red beet responded linearly to soil Zn and Cd, showing no sign of an uptake plateau.
Chang *et al.* (1997) found no evidence for either the time bomb hypothesis (no increase in soluble Cd with decreasing organic C content) or the plateau theory (the

Cd concentration in Swiss chard was proportional to the total Cd content in the soil) although in their long-term experiment all the necessary conditions for a plateau or a time bomb to take place were met. They proposed a new hypothesis which accounts for trace metals forming sparingly soluble metal solid phases before they are introduced into the soil. The rate of trace metal dissolution would then be surface limited and their absorption would depend on the dissolution kinetics of sludge-born metals. Higher sludge inputs would thus result in a larger solid-liquid interface and hence in more metals being available for plant absorption.

Requirements for dynamic modeling of heavy-metal flows in agro-ecosystems

For realistic balance calculations, information is needed about the partitioning of heavy-metal input between uptake, leaching and accumulation. Improving system understanding and predictive ability requires integration of model development, field and laboratory experimentation, and performance monitoring of the system studied (Jakeman *et al.*, 1993). Cameron *et al.* (1997) proposed to set up research and monitoring programs in which waste and soil characteristics and processes that determine both the fate of wastes in the soil and their impact on other environmental compartments are studied.

Key variables that should be monitored could be gathered by systematic, sequential sampling over extended time periods using 'adequate' monitoring networks and 'representative' agro-ecosystems. Adequate means that reliable and standardized controls and analytical methods are used. Representative means, among others, that both comparable and different soil types are studied and that different agricultural practices are represented in the monitoring network. In this way, the gathered data give information about the environmental pressure and performance of different systems. Although data from long-term field experiments are needed to study the long-term environmental consequences of applying fertilizers and soil conditioners (cf. McBride, 1995), they may not give sufficient information because variation in data collection may hamper the reliability of data and it may be difficult to maintain relevance for current agricultural practices due to changing practices, technologies, cultivars and natural variation. Also, it is hard to account for differences due to lateral transfer (runoff), development of macropores (leaching, preferential flow), fixation (gradual immobilisation), 'biodynamic accumulation', etc. These processes lead to the question how long a time trend is actually needed to arrive at proper conclusions.

The use of projective models is necessary to asses environmental consequences of different management practices (Bouma, 1997). The balance approach may thus be used in a strategy that advocates the prevention of future problems. A fundamental constraint of the balance approach, however, is that dynamic balance studies generally consider the soil composition and the values of the input and output rate coefficients to be constant in time. Because the soil composition and properties may change in time, the values of the output rate coefficients may not be constant at all since they can undergo significant changes in time as well. Also, the value of the input rate is expected to change in time due to changing deposition, application rates, and composition of soil amendments. This temporal variability should be taken into account in modeling of long-term heavy-metal behavior in the soil-plant system. In view of the variability of soil quality in space and time, the value of balance calculations that do not account for these variations might be questioned. However, more refined approaches are difficult to develop and to put into practice. As stated by Johnston & Jones (1995), "the resolution of the concerns regarding heavy metals requires that heavy-metal balance sheets are measured rather than estimated for a range of soils and cropping systems where aerial inputs, leaching losses, and changing soil metal availability with time are monitored". This means that dynamic modeling has to account for changing values of input and output rate parameters to enable proper interpretation of accumulation (total contents) versus effects. Only by long-term monitoring it is possible to measure the magnitude and the direction of changes in soil properties which may have consequences for heavy-metal availability and mobility.

In order to determine uncertainties, an uncertain variable should be described by a probability distribution and not by a single number. In that way, the range of outcomes may be associated with levels of probability of occurrence. Boekhold & Van der Zee (1991) carried out a sensitivity analysis for a dynamic Cd balance. In their analysis, both soil chemical and soil physical heterogeneity affected predicted Cd behavior considerably. Soil heterogeneity not only caused higher average accumulation of Cd as compared with predicted Cd contents for the corresponding homogeneous case, but also implied variability in output parameters to such an extent that average values alone did not contain enough information for a proper quality assessment. They derived the relative sensitivity functions for each rate parameter assuming that these were time invariant. In this paper, however, we argue that input and output rate parameters may vary to a large extent in both time and space. As a result, the probability distributions of the input and output parameters involved may change in time. Therefore, not only the likelihood of occurrence of parameter values within a distribution is important, but also the likelihood of a shift of the probability distribution function as a whole (changing trends) should be considered.

To estimate the probability distributions of the input and output rate parameters, very diverse information is needed. Product information (*e.g.*, on heavy-metal contents in soil amendments), management information (*e.g.*, fertilization regime, land use characteristics), and deposition inventories are required to determine an accurate input rate parameter distribution. Also, the partition of heavy metals between inert and labile forms (speciation) in soil amendments should be known. Information on soil properties (*e.g.*, composition, sorption parameters), climatic factors (*e.g.*, radiation, temperature, precipitation), and crop uptake dynamics (*e.g.*, crop rotation, uptake coefficient) are needed to estimate a crop uptake rate coefficient distribution. Tillage affects pH, organic matter and nutrient stratification in the soil profile (Grant & Baily, 1994) and may also affect soil microclimate, root distribution, and crop growth dynamics (Grant *et al.*, 1998). This kind of factors should be accounted for. Information about changes in sorption capacity, soil texture, soil water holding capacity, irrigation water (amount and quality), salinity, CEC and pH is needed to calculate the possible values of the leaching rate parameter. Irrigation is often used on high value food crops in (semi-) arid areas, where intensive use of fertilizers and soil amendments may introduce significant amounts of heavy metals in soil. Irrigation water itself mostly will not introduce large amounts of heavy metals to the system. However, irrigation water quality can have a marked influence on metal behavior in soil through complexation reactions with anions in the applied water (Grant *et al.*, 1998).

Bouma (1997) pleads for establishing 'research chains' in which a holistic, interdisciplinary analysis of a problem to be studied is followed by reductionistic basic research in relevant areas. Results from this basic research are then communicated to and analyzed by a holistic team to be integrated in the overall analysis. This 'two-way street' involves up- and down-scaling. A challenging task for such research chain would be to quantify the environmental and economic implications of variabilities of heavy-metal flows in agro-ecosystems in space and time. In that way also a coupling with environmental effects and with economic analyses that express the environmental effects of heavy-metal management in monetary terms could be realized.

Conclusion

The soil-crop system is dynamic in space and time. It is subject to short-term fluctuations and at the same time undergoing (gradual) long-term alterations. Changes in soil properties affect the form and availability of metals and need to be considered in the management of agricultural soils.

Textural changes in the soil induced by the organic amendments on the 'Van Bemmelenhoeve' appeared to be small. The fields with organic amendments (except for straw) show increased heavy-metal contents in the soil compared with the mineral field. The compost field and the mineral field have the highest and the lowest heavy-metal contents, respectively. Despite relatively high soil Cd contents in the compost field soil, Cd uptake in the field (potato leaf) and in the bio-assay with Swiss chard was low on this soil. Very likely Cd/Zn interaction plays an important role with respect to Cd uptake by crops on the compost field. Although compost amendments have increased the soil Cd contents, crop uptake is not determined by total contents only.

Dynamic heavy-metal balances are useful for projective purposes. Further dynamisation of balance models would be made possible if requirements are met that enable the quantification of probability distribution functions of the input and output rate parameters. Data needed for further dynamisation could be gathered by setting up research and monitoring programs with regard to the fate of heavy metals in agro-ecosystems and other (economic) sectors of society.

Also, research chains in which basic research (using refined models and basic data) and holistic research (using generic models and 'lumped' parameters) are coupled should be established. In that way also a coupling with environmental effects and with economic analyses of the management of heavy metals in agro-ecosystems could be realized.

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CHAPTER 11

EPILOGUE

In this chapter, the main conclusions and recommendations are presented.

Substance policy requires an integrated examination of substance flows through economy and environment relating problem flows in the environment to economic processes. In this thesis, balance calculations are used to determine the contribution of different input and output flows to heavy-metal accumulation in agricultural soil.
The scale on which processes are studied may influence the outcomes significantly. Heavy-metal balances on a national scale show the most important flows and bottlenecks, but neglect spatial variation of input/output flows. Although this limits the meaning with regard to environmental analysis, valuable information for economic and policy analyses may still be provided.
Whereas the controlling measures that are based on direct economic instruments or generic regulations often ignore farm characteristics and individual management options, field-scale and farm-gate balances give farmers specific feedback on effective options for a better heavy-metal management. Such specific analyses are needed due to great differences for different metals among and within farming systems. Incorporation of heavy-metal balances in a farm's environmental management system could be enhanced by company certification.
Heavy-metal behavior in the plough layer determines the resulting partitioning between accumulation in the topsoil, leaching to the subsoil (output to the environment), and crop uptake (output with produce). Balance sheets for the plough layer of individual fields thus provide site specific information and enable a direct link with criteria for soil protection and other environmental compartments. If large differences exist among fields due to differential management, large discrepancies may be expected between farm-gate and field-scale balances. Field-scale balances enable field specific and dynamic analysis of heavy-metal accumulation, leaching and uptake and consequently identification of 'hot spots' (*e.g.*, specific fields, crops, applications). Moreover, analyses on field scale enable elucidation of the role of internal cycles and the quantification of soil-bound heavy-metal flows like dirt tare and erosion.
Both the static and dynamic balance approaches as applied thus far lack an analysis of the effect of soil amendments on soil composition. However, soil composition determines soil bulk density and plough layer weight and hence the resulting change in heavy-metal content. It is therefore important to understand and account for the processes that affect soil composition.
The dynamic soil composition balance (DSCB) approach is presented as a way to calculate mass balances of both heavy metals and main soil constituents. Comparing results of the dynamic soil composition balance with those of the static and dynamic balance approaches reveals the necessity to account for changes in soil composition and for the effect of soil-bound heavy-metal flows when calculating heavy-metal accumulation in agricultural soil. This new balance approach is of special relevance if organic soil amendments (*e.g.*, manure and compost) and soil-bound heavy-metal

flows (*e.g.*, erosion) are involved. The practical implications of using the DSCB-approach for setting appropriate standards and for substance and material flow analyses should be further assessed.

Crop rotation and fertilizer choice influence the heavy-metal balance of arable farming systems significantly. In dairy farming systems, the role of feed management is very important. Mixed farming systems compare favorably with specialized (arable or dairy) farming systems with regard to heavy-metal accumulation. Due to the internal cycling of feedstuff and manure, less inputs are required than in specialized dairy farming systems and thus the import of heavy-metal containing raw materials and products is smaller. Mixed farming need not be restricted to farm level. Optimization of energy and material use and minimization of waste production may be enhanced by 'mixed farming' on a regional scale. In that case, different types of enterprises (agricultural, industrial, recycling) collaborate strategically to use effluents of one process as input for another. A reduction in the use of off-farm inputs can thus be realized by a move towards mixed livestock and cropping systems, which are more closed than specialized (arable and dairy) farms.

Calculations based on measurements at an experimental farm in the Cremona district in Italy reveal that although current application rates of sewage sludge and Bordeaux mixture (a mixture of copper sulphate and lime used as a fungicide) comply with European and Italian legal limits, groundwater and soil standards are likely to be exceeded. Because sewage sludge is regarded as waste, its use is subject to quality and application limits. Because Bordeaux mixture is regarded as protective agent its use is not restricted. In organic vineyards, no organo-pesticides are applied and thus Bordeaux mixture is used only. This results in much higher Cu application rates than in the case of combined Bordeaux mixture and organo-pesticide applications. Severe Cu contamination of integrated and especially organic vineyards is unavoidable with the currently allowed application rates of Bordeaux mixture. The results suggest that the current Italian soil protection policy as well as the EU policy are inconsistent and not conducive of a sustainable heavy-metal management of agricultural soils.

Balance approaches developed so far do not account for speciation of heavy metals in solution. However, speciation may be calculated and incorporated in the balance calculations if well defined speciation models are available. The consequences of changing land use from arable land to forestry with regard to Cu mobility, bioavailability, and accumulation in a sandy soil were studied by incorporating the Two Species Freundlich equation into a dynamic Cu balance of soil. The results show that Cu speciation changes dramatically with far reaching consequences for mobility and bioavailability. An interesting question that remains to be answered in the context of land use change is whether agricultural soil is part of the economy or part of the environment.

The concept of 'zero accumulation' of heavy metals in soil is not very manageable in practice. Therefore, sustainability indices (derived from the dynamic balance) are proposed as indicators of adverse effects of current agricultural practices and to assess the effects of different management options that aim at preventing quality standards from being exceeded. Moreover, they enable screening and comparing different agro-ecosystems without having to know all processes in detail and thus allow for a proper assessment of different farming systems that may reveal:

1) which heavy metal may cause the largest violation of standards (prioritization among different metals);

2) which environmental compartment is threatened most at steady state and for which compartment problems may be expected first;

3) which experimental data assessment should have priority in view of decreasing uncertainty and optimizing predictions;

4) which approaches to avoid violation of standards are feasible and most effective.

Because prevention is better than cure, a long-term strategy promotes reduction of inputs. Although input reduction slows down the rate of accumulation in soil, the response to input reduction on soil quality in terms of lowering soil contents will generally be slow. Reducing inputs to soils results in the steady state being reached with lower total accumulation and lower output rates. Input reduction can be reached both by reducing the amount of heavy metals in source material (quality) and by reducing the amount of fertilizer or manure added to the soil (quantity).

The soil-crop system is dynamic in space and time. Consequently, dynamic modeling of heavy-metal flows has to account for changing values of input and output rate parameters to enable proper interpretation of total accumulation versus effects. Only by long-term monitoring it is possible to measure the magnitude and the direction of changes in soil properties which may have consequences for heavy-metal availability and mobility.

A sustainable management of heavy metals in agro-ecosystems would be enhanced by a number of further developments in different areas, which are introduced and discussed below.

Further development of scale aspects

Compatibility of different scales is needed for realistic scenario and policy analysis. To ensure compatibility of substance flow analysis on the farm, regional and national scales, a bottom-up approach is necessary. A 'research chain' approach is advocated in which basic research (using refined models and basic data) and holistic research (using generic models and 'lumped' parameters) are coupled. In that way, scale aspects are appreciated and it might be studied how aggregation (up-scaling) and des-aggregation (down-scaling) has to be carried out. In the mean time, the different approaches to assessing heavy-metal balances (*i.e.*, top-down/holistic research and bottom-up/basic research) may be used in a complementary way. With the one general trends are discovered and with the other site and farming system specific investigations can be carried out.

Further development of environmental management systems

Heavy-metal management should be incorporated into environmental objectives at the individual farm level through further developement of environmental management systems. In that way, it becomes an integral part of decision making and can be incorporated into the full range of company operations. Specific analysis on the farm scale is needed because aggregated results are not relevant for on-farm environmental analysis and management. Farm-gate balances show the contaminating potential as the net farm environmental load. However, registration at the farm gate does not preclude too high additions on the field scale. Field-scale balances enable a direct link with criteria for the protection of soil and other environmental compartments.

Incorporation of heavy-metal balance sheets in an environmental management system of individual farms may result in combining several categories of controlling measures, *i.e.*, information and extension, economic incentives, and legislative measures. Moreover, an environmental management system can be supported by material flow analysis (material approach), life cycle analysis (product approach), integrated chain management (process approach), and by 'mixed farming' at a regional level (region approach). Certification at company level enables environmental performance monitoring and might promote strategic cooperation between industrial, agricultural, and recycling companies. Optimization models could be used and (environmental and economic) accounting systems could be coupled in order to choose appropriate fertilizers and to enable specific and accurate registration of input and output flows. Required information on heavy-metal contents could be obtained by using product labels, receipts and additional sampling (manure). Introduction of product labels enables incorporation into materials and minerals registration and accounting systems in such a way that farmers can make their own choices.

Further development of indicators

With the sustainability indicators, quantitative evaluation of specific local situations and of characteristic 'general situations' can be carried out.

Combined indicators for economic and environmental performance are needed. By an integrated examination of flows through economy and environment, a whole-chain perspective is obtained and problem-shifting can be prevented. Coupling of environmental impact assessment (fate and risk) and economic impact assessment (trade-offs) enables definition of consistent measures to meet environmental and economic goals for different farming systems. An integrated sector plan should correspond with additional individual environmental management plans.

Further development of dynamic modeling

Dynamic heavy-metal balances are useful for projective purposes. Further dynamisation would be possible if requirements were met that enable the quantification of probability distribution functions of the input and output rate parameters. Probability distribution functions of the input and output rate parameters may be subject to temporal changes. Therefore, not only the likelihood of occurrence of parameter values within a distribution is important, but also the likelihood of a shift of the probability distribution function as a whole should be considered. To estimate the (probability distributions of the) input and output rate parameters, very diverse information is needed. Product information (*e.g.*, on heavy-metal contents in soil amendments), management information (*e.g.*, fertilization regime, land use characteristics), and deposition information are required to determine an accurate input rate parameter distribution. Also, the partitioning of heavy metals between inert and labile forms in soil amendments should be known. Information on soil properties (*e.g.*, composition, sorption parameters), climatic factors (*e.g.*, radiation, temperature, precipitation), and crop uptake dynamics (*e.g.*, crop rotation, uptake coefficients) are needed to estimate leaching and crop uptake rate coefficient distributions.
Data needed for further dynamisation could be gathered by setting up research and monitoring programs with regard to the fate of heavy metals in agro-ecosystems and other economic sectors of our society.

Further development of monitoring

To validate dynamic balance models and to gather relevant information for field-scale assessment of proper heavy-metal management, experimental research should focus on long-term monitoring of heavy metals in soil, crops, and (groundwater) leachate. Only by long-term monitoring it is possible to measure the magnitude and the direction of changes in soil properties which may have consequences for heavy-metal availability and mobility.
Experimental farms are valuable objects for studying heavy-metal flows. Integral monitoring of nutrients, pesticide, energy, and heavy-metal flows at the farm gate is recommended to define sustainable management options for agro-ecosystems. An important issue that should be addressed in heavy-metal balance research is the development of suitable methods to quantify leaching from the plough layer.
Quality and quantity of data to be used in balance studies vary largely and both need to be improved to reduce uncertainties that are very large at the moment. Therefore research and monitoring programs should be set up in which characteristics and processes that determine both the fate of soil amendments in the soil and their impact on other environmental compartments are studied. Key variables could be gathered by systematic, sequential sampling over extended time periods using adequate monitoring networks and representative agro-ecosystems. Adequate means that reliable and standardized controls and analytical methods are used. Representa-

tive means, among others, that both comparable and different soil types are studied and that different agricultural practices are represented in the monitoring network.
Dynamic balance calculations can be carried out relatively simply if information is available about local application rates, soil and crop characteristics. Integration of model development, field and laboratory experimentation, and performance monitoring of the system studied enables improvement of system understanding and predictive ability which is needed to support proper decision making.

Further development of a coherent EU policy

Input reduction could be aimed at by legislation, economic instruments, technology and by changing management practices by educating farmers on how to use nutrient and heavy-metal balances. Harmonization of environmental quality standards and quality standards for produce (internationally and inter-compartmentally) is needed for input reduction to become a succesful strategy. Accumulation of heavy metals in agricultural soil can be prevented by achieving an input that is smaller than, or equal to, the 'total acceptable output'. This output is defined by crop offtake, leaching, and erosion. Maximum allowed offtake would be determined by statutory limit values of the metal contents in food crops and existing natural limitations on the mass of food crops that can be produced on a given area of land. Directives related to unwanted substances in animal feed have a similar effect on feed crops and thus also the amount of metal that is permitted to be taken up by feed crops is limited. Maximum permissible concentrations in drainage water or groundwater would determine allowed leaching losses.
National and regional monitoring networks for soil and groundwater quality are needed to carefully examine a country's practices and to determine the rate of input, output and accumulation regarding agricultural soils. Because there are large differences among different countries, regions, and agro-ecosystems across Europe, regional strategies for sustainable (heavy-metal) management of agro-ecosystems are needed instead of uniform measures. However, generic measures at the (inter)national level are required to enable proper procedures and measures with regard to product labeling, company certification, industry convenants, and import and trade (barriers).

Further development of an ethical foundation to support sustainable management of agro-ecosystems

Because a substantial part of heavy-metal inputs to agricultural soils results from atmospheric deposition and from applying waste materials, sustainable agriculture will demand changes in the way metals are handled in other sectors of the economy as well as in agriculture itself. 'Sustainable agriculture' requires more than just scientific solutions, technical modifications, and finetuning of conventional practices. Different societal values and objectives (ethical, political, environmental, economic, and administrative) need to be reconciled and integrated. In this respect, an interesting study on Amish farming and society was carried out by Stinner *et al.* (1989). Amish agriculture is vital because Amish culture sanctifies the virtues that make good farming an ecologically prudent practice: moderation, simplicity of life, frugality, neighborliness, family stability and financial common sense. Moreover, Amish culture provides a supportive community in which these values can flourish. This example teaches the importance of sustainable agricultural practices having a cultural base which includes a strong land stewardship ethic and a commitment to that ethical foundation on the part of all society members (Stinner *et al.*, 1989).

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SUMMARY

Sustainable management of heavy metals in agro-ecosystems

In 1993, the Netherlands Organization for Scientific Research (NWO) launched a priority research program on 'Sustainability and Environmental Quality'. Within this program, the METALS sub-program focusses on the accumulation of metals in economy (*e.g.*, zinc in gutters) and the environment (*e.g.*, soil), the mechanisms behind these processes, the associated risks, the possibilities for a sustainable management of metal flows, and their consequences for society and environment. This Ph.D. thesis has resulted from the research on sustainable management of heavy metals (cadmium, copper, lead, and zinc) in agro-ecosystems in the Netherlands and some other European countries.

Accumulation of heavy metals in agricultural soil may cause problems if certain levels are exceeded. The productivity of soil and quality of produce should be protected but at the same time the ecological functioning of the soil should not be damaged, nor should emissions from the soil adversely affect other environmental compartments (*e.g.*, groundwater). Heavy-metal cycles and input and output flows in agro-ecosystems have to be analyzed to identify the most important sources and processes that lead to accumulation. In order to determine the options for a sustainable heavy-metal management in agriculture, heavy-metal balance sheets are used as a means to quantify input (*e.g.*, fertilizers, deposition) and output (*e.g.*, leaching, crop offtake) flows in agro-ecosystems and to calculate resulting accumulation in soil. Heavy-metal balances of agro-ecosystems can be studied within the context of substance flow analysis (SFA), which is based on the law of conservation of mass. SFA consists of an integrated examination of all flows of a substance or a group of substances within a defined (geographic) system (Chapter 2).

Several European studies on heavy-metal balances on different spatial scales and in different agro-ecosystems are reviewed and implications for an effective heavy-metal management of agro-ecosystems are disussed. Heavy-metal balances on a national scale study the agricultural sector as a whole. Although their meaning is quite limited with regard to environmental and specific on-site management analyses, they give valuable information for economic analyses. The studies on heavy-metal balances in Denmark and Finland show that generic measures may be very fruitful. Generic measures at the (inter)national level are required to enable proper procedures and measures with regard to product labeling, company certification, industry convenants, and import and trade with regard to heavy metals. In order to be able to discover relevant options for an effective management of heavy metals in agro-ecosystems, heavy-metal balances on the farm and field scales should be used in addition. These heavy-metal balances could be incorporated in an environmental management system of individual companies (Chapter 3).

Quantification of the topsoil (or plough layer) balance can be carried out by different approaches *i.e.*, the static balance (SB), the dynamic balance (DB), and the dynamic soil composition balance (DSCB) approaches. In a SB approach, the output flows are assumed not to be related to the (total) metal content in the soil. The change in heavy-metal content in the plough layer is therefore the result of the net difference between input rate and (constant) output rates. Because a SB does not regard the dependency between soil content and output flows, it cannot realistically simulate the development of the heavy-metal soil content in time. For a simulation of the long-term behavior in time, a DB may be calculated in which the relationship between soil content and output flows in time are explicitly included. Information which is needed to calculate heavy-metal balance sheets on the field scale is shown and the (im)possibilities to aggregate results on the field scale to higher levels of analysis are discussed (Chapter 4).

Chapter 5 provides a detailed picture of the 'dynamic soil composition balance' (DSCB) approach which takes into account the composition of both soil amendments and soil when calculating heavy-metal accumulation in soil. The DSCB approach can be used to distinguish the effect of the matrix of soil amendments on the resulting accumulation in the plough layer. This new approach distinguishes heavy-metal input flows that are 'free' (*e.g.*, deposition, mineral fertilizers) and input flows that are 'bound' to a soil matrix (*i.e.*, associated with soil particles in amendments like compost). Also, a distinction is made between output flows that are 'free' (*e.g.*, leaching and plant uptake) and that are 'bound' (*e.g.*, soil adhering to crops and erosion).

Cadmium (Cd), copper (Cu), lead (Pb), and zinc (Zn) flows of arable, dairy and mixed farming systems in the Netherlands are studied. The crop rotation and the choice of fertilizers clearly influence the heavy-metal balance of arable farming systems. In dairy farming systems, the role of feed management is very important, but the effects on the heavy-metal balance are not always straightforward. Mixed farming systems compare favorably with specialized (arable or dairy) farming systems with regard to heavy-metal accumulation. Due to the internal cycling of feedstuff and manure, less inputs are required and thus the import of heavy-metal containing raw materials and products is minimized. Mixed farming need not be restricted to the farm level, because optimization of energy and material use and minimization of waste production may also be enhanced by 'mixed farming' at the regional level. Experimental farms are valuable objects for studying heavy-metal flows by carrying out measurements in agro-ecosystem's compartments. Integral monitoring of nutrient, pesticide, energy, and heavy-metal flows on the farm-gate scale is recommended to define sustainable management options for agro-ecosystems (Chapter 6).

Calculations based on data gathered at an Italian experimental farm reveal that the permitted annual application rates of sewage sludge and Bordeaux mixture in Italy pose problems for Cd, Cu, and Zn. Severe Cu pollution of integrated and especially organic vineyards is unavoidable with the currently allowed application rates of

Bordeaux mixture (a mixture of copper sulphate and lime used against mildew). The results suggest that the current Italian soil protection policy as well as the policy of the European Union (EU) are inconsistent and not conducive of a sustainable management of heavy metals in agriculture (Chapter 7).

By incorporating a well defined speciation model into a dynamic Cu balance of soil, it is possible to show the relative changes in availability and mobility due to increasing soil organic matter content and decreasing pH after changing land use from arable farming to forestry. Inter-species effects are shown to be very important (Chapter 8).

Sustainability indicators are introduced to assess the sustainability of current metal cycles in agro-ecosystems based on dynamic heavy metal balances for the plough layer. These characteristic numbers can be used as indicators for potentially adverse effects of current agricultural practices, since they account for quality standards for soil, produce, and groundwater. They can also be used to assess the effects of different management options that aim at preventing quality standards from being exceeded as they provide insight in the dynamics governing input-output relationships. These indicators serve for screening and comparing different agro-ecosystems without having to know all processes in detail and thus allow for a proper assessment on a relative basis. Such an assessment may reveal:

1) which heavy metal may cause the largest violation of standards;

2) which environmental compartment is threatened most and for which compartment problems may be expected first;

3) which experimental data assessment should have priority in view of decreasing uncertainty and optimizing predictions;

4) which approaches to avoid violation of standards (short-term or long-term strategies) are feasible and most effective.

The sustainability indicators indicate some points of action for heavy-metal policy and management, like setting up monitoring programs to carefully examine a country's practices and determining the rate of input, output and accumulation regarding agricultural soils. In this way, regional strategies for heavy-metal management could be developed (Chapter 9).

Literature and measurements with regard to long-term field experiments are interpreted and the options for calculating realistic dynamic heavy-metal balances of soil are discussed. Temporal variability of input and output rate parameters should be taken into account in modeling of long-term heavy-metal behavior in the soil-crop system to enable proper interpretation of total accumulation versus effects. Only by long-term monitoring is it possible to measure the magnitude and the direction of changes in soil properties which may have consequences for heavy-metal availability and mobility. Key variables could be gathered by systematic, sequential sampling over extended time periods using adequate monitoring networks and representative agro-ecosystems (Chapter 10).

To enhance sustainable management of heavy metals in agro-ecosystems, further development is recommended with respect to scale aspects, environmental management systems, economic and environmental indicators, dynamic modeling, and monitoring. Furthermore, a coherent EU policy and the development of an ethical foundation are needed to advance sustainable agriculture (Chapter 11).

SAMENVATTING

Duurzaam beheer van zware metalen in agro-ecosystemen

In 1993 lanceerde de Nederlandse Organisatie voor Wetenschappelijk Onderzoek (NWO) een prioritair onderzoeksprogramma gericht op "Duurzaamheid en Milieukwaliteit". Binnen dit programma stelt het METALEN-subprogramma de accumulatie (ophoping) van metalen in economie (bijvoorbeeld zink in dakgoten en koper in waterleidingen) en milieu (bijvoorbeeld in de bodem) centraal. De mechanismen achter deze accumulatie, de gerelateerde risico's, de mogelijkheden voor een duurzaam beheer van metalenstromen, en de gevolgen daarvan voor samenleving en milieu zijn hierbij van belang. Dit proefschrift is het resultaat van onderzoek naar duurzaam beheer van zware metalen (cadmium, koper, lood en zink) in agro-ecosystemen (landbouwsystemen) in Nederland en in enkele andere Europese landen.

Accumulatie van zware metalen in cultuurgrond kan problemen veroorzaken als bepaalde gehalten overschreden worden. De produktiviteit van de bodem en de kwaliteit van produkten behoeven bescherming. Tegelijkertijd mag het ecologisch functioneren van de bodem niet geschaad worden en ook zouden emissies vanuit de bodem geen nadelige effecten op andere milieucompartimenten (bijvoorbeeld grondwater) tot gevolg mogen hebben. Kringlopen en toe- en afvoerstromen van zware metalen in agro-ecosystemen moeten geanalyseerd worden om de belangrijkste oorzaken van accumulatie te achterhalen. Om de opties voor een duurzaam zware-metalenbeheer in de landbouw na te gaan, worden zware-metalenbalansen gebruikt om toevoer- (bijvoorbeeld bemesting en depositie) en afvoerstromen (bijvoorbeeld uitspoeling en gewasafvoer) in agro-ecosystemen te kwantificeren en om de resulterende accumulatie in de bodem te berekenen. Zware-metalenbalansen van agro-ecosystemen kunnen bestudeerd worden in de context van stofstroomanalyse. Stofstroomanalyse is gebaseerd op de wet van behoud van massa en is gericht op geïntegreerd onderzoek naar alle stromen van een bepaalde stof of groep van stoffen binnen een gedefinieerd (geografisch) systeem (Hoofdstuk 2).

Er is een overzicht gemaakt van verscheidene Europese studies naar zware-metalenbalansen op verschillende ruimtelijke schaal en in verschillende agro-ecosystemen. De implicaties hiervan voor een effectief zware-metalenbeheer worden besproken. Zware-metalenbalansen op nationale schaal bezien de agrarische sector als één geheel. Hoewel de betekenis van nationale studies vrij beperkt is met betrekking tot analyses op het gebied van milieu-effecten en opties voor locaal management, geven ze wel waardevolle informatie voor economische analyses. De studies naar zware-metalenbalansen in Denemarken en Finland tonen aan dat generieke maatregelen zeer vruchtbaar kunnen zijn. Generieke maatregelen op (inter)nationaal niveau met betrekking tot zware metalen in bedrijfsvoering, produkten en grondstoffen zijn noodzakelijk om geschikte procedures en maatregelen mogelijk te maken op het gebied van productlabels, bedrijfscertificatie, convenanten met de industrie en import en handel. Om relevante opties voor een effectief beheer van zware metalen in agro-ecosystemen te ontdekken, zouden ook zware-metalenbalansen op bedrijfs- en veldschaal gebruikt moeten worden. Deze zouden geïncorporeerd kunnen worden in een milieumanagementsysteem van individuele bedrijven (Hoofdstuk 3).

Het kwantificeren van een zware-metalenbalans van de bovenste laag van de bodem (de bouwvoor) kan op verschillende manieren uitgevoerd worden en wel volgens de statische-balans- (SB), de dynamische-balans- (DB) en de dynamische-bodemsamenstellingsbalans- (DBB) benaderingen. In een SB-benadering wordt verondersteld dat de afvoerstromen niet gerelateerd zijn aan het (totale) zware-metalengehalte in de bodem. De verandering in zware-metalengehalte in de bouwvoor is dan ook het resultaat van het netto verschil tussen toevoersnelheid en (constante) afvoersnelheden. Omdat een SB de relatie tussen het gehalte in de bodem en de afvoerstromen niet in beschouwing neemt, kan deze balansberekening de ontwikkeling van het zware-metalengehalte in de bodem in de loop van de tijd niet op een realistische manier simuleren. Ten behoeve van een lange-termijnsimulatie kan een DB berekend worden die de relatie tussen bodemgehalte en afvoerstromen in de tijd wel expliciet verdisconteert. De informatie die nodig is om zware-metalenbalansen op veldschaal te berekenen en de (on)mogelijkheden om de resultaten te aggregeren van veldschaal naar hogere niveaus van analyse worden besproken (Hoofdstuk 4).

In Hoofdstuk 5 wordt uitgebreid ingegaan op de dynamische-bodemsamenstellingsbalans (DBB). Deze benadering neemt zowel de samenstelling van de bodem als van de materialen die aan de bodem toegevoegd worden in beschouwing bij het berekenen van zware-metalenaccumulatie in de bodem. De DBB-benadering kan gebruikt worden om het effect van de matrix waarin de metalen worden toegevoegd op de resulterende accumulatie in de bouwvoor duidelijk te maken. Deze nieuwe benadering onderscheidt toevoerstromen van zware metalen die "vrij" zijn (bijvoorbeeld depositie, kunstmeststoffen) en die "gebonden" zijn aan een bodemmatrix (geassocieerd met gronddeeltjes in toevoegingen zoals compost). Bovendien wordt er een onderscheid gemaakt tussen afvoerstromen die "vrij" zijn (bijvoorbeeld uitspoeling en gewasafvoer) en die "gebonden" zijn (bijvoorbeeld tarra, aan gewas klevende grond, en erosie).

In Hoofdstuk 6 worden stromen van cadmium (Cd), koper (Cu), lood (Pb) en zink (Zn) bestudeerd in akkerbouw, melkveehouderij en gemengde bedrijfssystemen in Nederland. De vruchtwisseling en de meststoffenkeuze hebben een duidelijk effect op de zware-metalenbalans van akkerbouwsystemen. In de melkveehouderij speelt het voederregime een belangrijke rol, maar de effecten op de zware-metalenbalans zijn niet eenduidig. Gemengde systemen onderscheiden zich in gunstige zin van gespecialiseerde (akkerbouw of melkvee) landbouwbedrijven. Ten gevolge van de interne stromen van voeder en mest is minder toevoer nodig van grondstoffen en producten die zware metalen bevatten. Gemengde landbouw hoeft niet beperkt te blijven tot de schaal van de boerderij, omdat optimalisatie van het gebruik van energie en materialen en minimalisatie van afvalproductie ook bevorderd kunnen worden door middel van "gemengde bedrijfsvoering" op regionale schaal.

Proefboerderijen zijn waardevol voor het bestuderen van zware-metalenstromen door de mogelijkheid om ter plekke metingen in verschillende compartimenten uit te voeren. Integrale monitoring van nutriënten-, pesticiden-, energie-, en zware-metalenstromen op bedrijfsniveau wordt aanbevolen om opties na te gaan voor een duurzaam beheer van agro-ecosystemen (Hoofdstuk 6).

Berekeningen gebaseerd op gegevens die verzameld zijn op een Italiaanse proefboerderij, tonen aan dat de in Italië toegestane jaarlijkse toevoer van zuiveringsslib problemen oplevert ten aanzien van Cd, Cu en Zn. Ernstige verontreiniging met Cu is onvermijdelijk in geïntegreerde en zeker in biologische wijngaarden met de huidige toegestane toediening van Bordeause pap (een mengsel van kopersulfaat en kalk dat gebruikt wordt tegen meeldauw). De resultaten suggereren dat het huidige bodembeschermingsbeleid van zowel Italië als de Europese Unie niet consistent is en ook niet leidt tot een duurzaam beheer van zware metalen in de landbouw (Hoofdstuk 7).

Door een goed gedefinieerd chemische-speciatiemodel in te bouwen in een dynamische Cu-balans van de bodem is het mogelijk om relatieve veranderingen te tonen in beschikbaarheid en mobiliteit van Cu ten gevolge van een toename van het organische-stofgehalte van de grond en een daling van de pH na landgebruiksverandering van akkerbouw naar bosbouw (Hoofdstuk 8).

Duurzaamheidsindicatoren, die gebaseerd zijn op dynamische zware-metalenbalansen van de bouwvoor, worden geïntroduceerd om de duurzaamheid van huidige metalencycli in agro-ecosystemen te beoordelen. Deze kentallen kunnen gebruikt worden als indicatoren voor potentieel nadelige effecten van landbouwkundige praktijken, doordat zij kwaliteitsnormen voor bodem, producten en grondwater in beschouwing nemen. Ze kunnen ook gebruikt worden om de effecten vast te stellen van verschillende managementopties die erop gericht zijn overschrijding van kwaliteitsnormen te voorkomen, doordat ze inzicht verschaffen in de dynamische relaties die de verhouding tussen toevoer en afvoer bepalen. De indicatoren dienen als middel om verschillende agro-ecosystemen te vergelijken zonder alle processen in detail te hoeven kennen. Zo maken ze het mogelijk vast te stellen:

1) welk zwaar metaal tot de grootste overschrijding van normen kan leiden;

2) welk milieucompartiment het meest bedreigd wordt en voor welk compartiment problemen het eerst verwacht kunnen worden;

3) welke experimentele dataverzameling prioriteit verdient met het oog op verminderen van onzekerheden en optimaliseren van voorspellingen;

4) welke aanpak om overschrijding van normen te vermijden (korte-termijn- of lange-termijnstrategieën) het meest geschikt en effectief zijn.

De duurzaamheidsindicatoren wijzen op concrete mogelijkheden voor zware-metalenbeleid en -management zoals het opzetten van monitoringsprogramma's om de praktijken van een bepaald land nauwkeurig in kaart te brengen en de snelheden van toevoer, afvoer en accumulatie ten aanzien van cultuurgrond te bepalen. Op die manier zouden dan regionale strategieën voor zware-metalenbeheer ontwikkeld kunnen worden (Hoofdstuk 9).

Literatuur en metingen met betrekking tot langlopende veldexperimenten worden geïnterpreteerd en de mogelijkheden voor berekening van realistische dynamische zware-metalenbalansen van de bodem worden besproken. Temporele variabiliteit van toevoer- en afvoersnelheidsparameters zouden in beschouwing genomen moeten worden bij het modelleren van het lange-termijngedrag van zware metalen in het bodem-gewassysteem om een juiste interpretatie van totale accumulatie versus effecten mogelijk te maken. Alleen door lange termijn monitoring is het mogelijk om de grootte en richting te meten van veranderingen in bodemeigenschappen die gevolgen kunnen hebben voor de beschikbaarheid en mobiliteit van zware metalen. De belangrijkste variabelen zouden verzameld kunnen worden door systematische en sequentiële monstername gedurende lange perioden met gebruik van adequate monitoringsnetwerken en representatieve agro-ecosystemen (Hoofdstuk 10).

Om een duurzaam beheer van zware metalen in agro-ecosystemen te bevorderen, wordt een verdere ontwikkeling aanbevolen op het gebied van schaalaspecten, milieumanagementsystemen, economische en milieu-indicatoren, dynamische modellering, en monitoring. Bovendien dient aandacht te worden besteed aan de samenhang in het EU-beleid en aan de ethische grondslag waarvan de ontwikkeling van duurzame landbouw (mede) afhankelijk is.

Curriculum Vitae

Simon Willem Moolenaar werd op 22 oktober 1968 geboren te Leiden. Hij groeide op als de jongste van vier kinderen in het gezin van Rob en Atie Moolenaar. Drie jaar kleuterschool legde een stevige basis voor de verdere schoolcarrière. Na twee jaar klassikaal onderwijs aan de lagere school te Sassenheim zette hij de opleiding voort aan een jenaplan school te Blokker. Na deze cultuurschok dapper doorstaan te hebben, ving hij aan met de brugklas van "S.G. Werenfridus" te Hoorn. Na de vierde klas van het Gymnasium ging hij verder met het Atheneum. Met het Atheneum-B diploma op zak vertrok hij naar Wageningen, het mooie stadje aan de Rijn, met de vraag of hij daar Moleculaire wetenschappen of Milieuhygiëne zou gaan studeren. Na de propaedeuse Moleculaire wetenschappen koos hij alsnog voor de studie Milieuhygiëne met als oriëntatie bodemkwaliteitsbeheer. Na het afstudeervak Microbiologie, ging hij een jaar op stage bij het United States Environmental Protection Agency (Kerr laboratory, Ada, Oklahoma, USA). Na deze enerverende tijd, begon hij aan het afstudeervak Bodemhygiëne en -verontreiniging. De studie werd in 1993 *Cum Laude* afgerond. Vrijwel aansluitend zette hij het werk bij de vakgroep Bodemkunde en Plante(n)voeding voort in de vorm van een detachering als NWO-OIO. De Nederlandse Organisatie voor Wetenschappelijk Onderzoek (NWO) financierde namelijk een onderzoeksproject op het gebied van "duurzaam beheer van zware metalen in de landbouw" waar hij als Onderzoeker in Opleiding van 1 november 1993 tot 1 januari 1998 aan mocht werken. De resultaten van dit promotie-onderzoek heeft hij opgeschreven in het onderhavige proefschrift. Sinds januari 1998 is hij werkzaam bij het milieu-adviesbureau IWACO.