Soil and Water

Integrated

Protection

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Risks from Diffuse Pollution

Research needs defined by SOWA

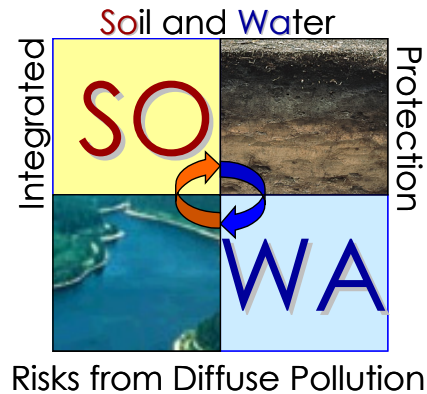**Authors:** *Dietrich Halm (D), Peter Grathwohl (D)* – editors

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Preface

Diffuse distribution of chemical substances is ubiquitously occurring including urban spaces as well as rural regions. Industrial development has brought prosperity to millions of people, but has also left a legacy of environmental damage that continues to impact natural resources and ultimately the human well-being. A wide range of man-made chemicals designed for use in industry, agriculture, pest control, consumer goods and emissions from the combustion of fossil fuels are the main sources for diffuse pollution of soils. Soil pollution and thus degradation is therefore a result of population growth and technological development. Within the water cycle, soils act as the key zone for storage, filtration and transport of water and associated pollutants (Fig. 1). If the accumulation of pollutants exceeds the buffer capacity, then soils or sediments can become a source of diffuse pollution releasing pollutants to adjacent compartments such as groundwater and surface waters. This is recognised in the EU Soil Thematic Strategy (DG ENV - *Towards a Thematic Strategy for Soil Protection*, COM(2002), 179 final) where diffuse pollution is itemised as a threat to the soil by direct or indirect pollution due to the disposal/use of sewage sludge, incineration sludge, compost and pesticides. SOWA focuses on the risks from diffuse pollution of soils leading to a damage of crucial soil functions such as:

- Base for ecosystem quality, sustainable land use and safe food production

- Filter for drinking water

- Sink/source for anthropogenic and natural pollutants

A general problem of diffuse pollution is that is often invisible in contrary to local hazards. Generally, the diffuse input of pollutants into soils of a rural landscape is low and therefore, the burden from diffuse sources is either not realised or seen as a "normal" situation and a gradually increasing concentration of pollutants in soils escapes most common monitoring tools.

The leitmotif of SOWA was that soil has to be recognised as a key compartment in the water cycle. The most relevant scientific questions for future research addressing the physic-chemical multi-functionality of soils, long-term *vs.* short term issues and European/global scale opposed to local dimensions were evaluated in SOWA.

With totally 9 different disciplines involved (soil science, soil chemistry, soil physics, hydrogeology, water resources management, agricultural sciences, environmental chemistry, analytical chemistry, environmental/civil engineering) SOWA provided a multidisciplinary forum of experts for the identification of research needs and strategies for integrated soil and water protection. The research needs and strategies were defined in five thematic working groups:

1) **Inventory** of priority compounds and trends

2) Screening and monitoring **tools** at different scales

3) Chemical and physical **processes** in the unsaturated soil zone

4) Heterogeneity and **scale issues** in soil and groundwater

5) Diffuse soil and groundwater pollution: Monitoring, remediation and **management** options
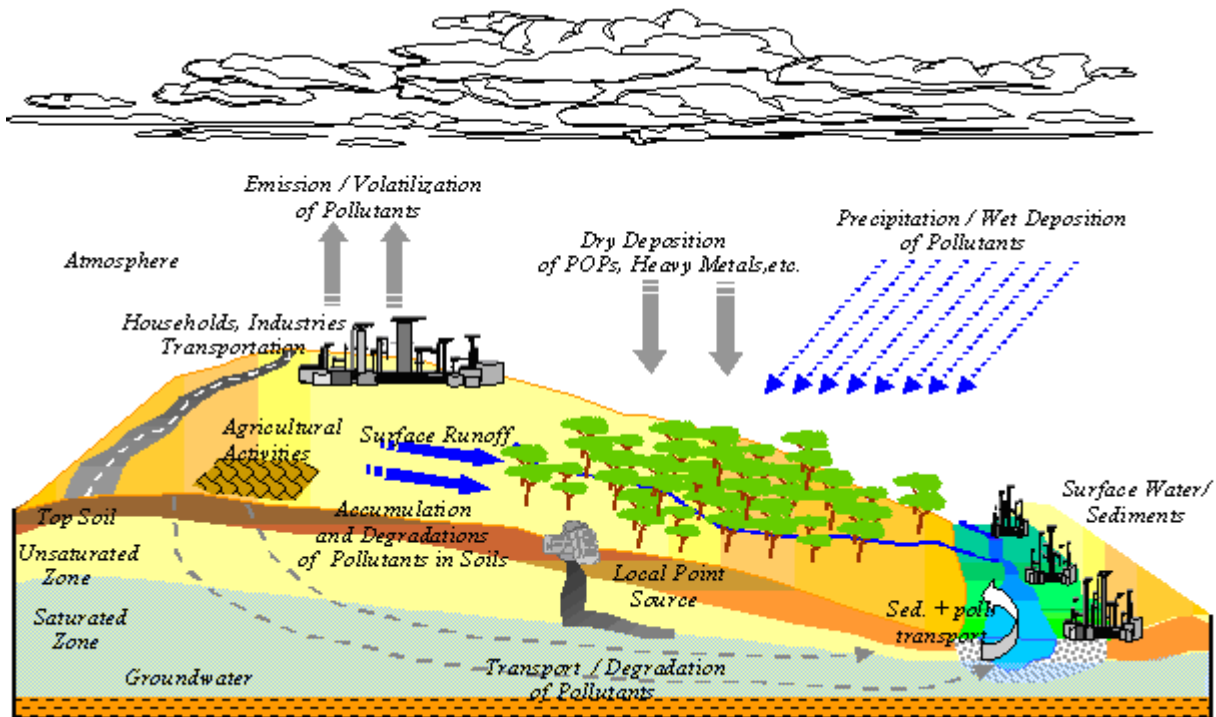
Figure 1: The pressure of diffuse pollution on soils: polluted soils will eventually loose their important function as filter and buffer in the water cycle. Soils are the key element in the water cycle determining the quality of groundwater, surface water, and finally drinking water

The SOWA Joint Document provides the results of five thematic working groups on the future challenges in research towards integrated soil and water protection. It contains a range of questions asking e.g. for suitable ways how to identify potentially dangerous chemicals in future or for management options of soil and water pollution at different scales incl. socio-economic issues. In addition, the document includes results from two international SOWA-Workshops, held in Tübingen (Halm and Grathwohl, 2003) and in Prague (Halm and Grathwohl, 2004) as well as invited statements from internationally leading experts in this field. The workshops had 85 and 47 participants, invited speakers included.

The first five thematic chapters correspond to the five SOWA working groups which at the same time correspond to the workpackages of SOWA. After an introduction, the chapters discuss the state of the art and point out research needs for future challenges and conclusions. Annexed to each chapter, text-boxes in yellow summarise the most crucial scientific questions which were identified by the authors. In special blue text-boxes, external experts state their personal view and the most urgent lacks in reseach they see to be addressed in future. Chapter 6 extracts conclusions from chapter 1 to 5.

Tübingen, January 2005

Dietrich Halm and Peter Grathwohl (Editors)

0   Introduction

Contamination of our natural resources, such as atmosphere, water, and eventually soil have received much attention in the past decades. Whereas locally contaminated sites for a long time received prime attention, diffuse pollution was until recently not recognised as major threat for soil, water, and the atmosphere. Generally, the fact that contamination requires management and remediation has been a major incentive for several EU framework research programmes. During the past decade, limits to the funds available for active remediation have become increasingly recognised in the member states of the European Union. As a result, environmental policies focussed less on the development of new remedial technologies and more on appropriate risk management strategies and pollution prevention. The risk-based land management approach - where key concepts in risk analysis are biological availability and mobility of contaminants - is not only a change in perception, but also a change in nuances to be considered (Vegter et al., 2002).

Inventory. During the last decades, large amounts of different chemicals were released to the environment through industrial waste, agricultural practice (including manure, sewage sludge and organic waste applications) and discharges from wastewater treatment plants. This contamination can have a serious impact on ecosystems due to their strong activity at low doses. According to an inventory of priority compound classes, persistent organic pollutants (POPs) have been identified to exhibit potentially harmful effects to man and the environment. In addition to being persistent, POPs are typically lipophilic and therefore bio-accumulative, and toxic (pbt: persistent, bioaccumulative and toxic). Currently, a second wave of pollutants, the so-called emerging contaminants are suspected of causing adverse effects in both humans and wildlife. In addition, intermediates and end-products of the chemical and pharmaceutical (incl. veterinary) industry have to be considered as potential pollutants. One of the key issues with emerging contaminants is that although few of them have been recently subject to legislation, many potentially dangerous compounds are not yet recognised and as a consequence no routine monitoring programmes exists. One of the key issues is the evaluation of risks of such non-regulated chemicals that are currently being detected in the environment.

Processes. Studies regarding biological availability and mobility have often resulted in different and apparently contradictory observations and conclusions. However, the underlying physico-chemical processes cannot be in conflict and therefore such contradictions have to be due to limitations in process understanding. Such apparent contradictions lead to uncertainties which may be a major constraint for the development accurate policies for management of contamination. The awareness of the importance and complexity of these processes controlling the subsurface contaminant transport and the contaminant fate in soils increases. The complexity arises from several sources. First of all, the soil itself is a complicated disperse system made up of a microscopically heterogeneous mixture of solid, liquid and gaseous phases. The solid phase contains mineral and organic particles of varying sizes, shapes and chemical composition ranging from molecular-sized and colloidal particles to coarse sand and gravel. The organic fraction of the solid phase includes diverse communities of living organisms, plant and animal residues in different stages of decomposition and humification as well as various types of coals and charred organic matter. How soil reacts to long-term changes in the hydrological cycle or by changes in land use is still not understood in its complexity (weathering, dissolution / precipitation of minerals, carbon turnover, release of DOC, wetting and drying properties, permeability…).

Scales. One of the major causes for uncertainty and erroneous understanding of causal relationships and the magnitude of parameters and trends has been identified as being the 'scale problem'. Different levels of heterogeneity are encountered when passing from the microscopic to the macroscopic scale. The scale problem is due to the spatiotemporal (i.e., in space and in time) variability of the systems of interest: statements that concern a particular scale may (and often will) not hold at other scales. Hence, extrapolation of understanding to a larger or to a smaller scale may require additional knowledge at these larger or smaller scales. If this need for additional knowledge is not recognised, the implicit assumption of 'scale invariance' is made and if this assumption is false, the interpretation of measurements or of model exercises may be erroneous.

Monitoring. During the last decade, the need for new, fast, and cost effective environmental screening and monitoring methods has grown significantly. Regional and larger scale screening and monitoring require balloon, aircraft or satellite based remote sensing. Research is needed to uniquely relate the measured quantity with type and levels of pollution and to resolve measurement uncertainty. This, of course, will require the identification of suitable and pollution specific indicators (e. g. magnetic proxies), which can be measured much easier and allow pollution pattern mapping as well as the monitoring of pollution dynamics and thus the early identification of long-term trends of increasing pollution.

Management. Presently, diffuse pollution of soils and water is addressed by sectorial approaches. Water or soil protection usually focus on their specific domains and do not sufficiently coordinate their efforts. This is also reflected in legislation and regulation. Different laws deal with to soil and water protection. As chemicals are cycling in the environment between different compartments, problems in one compartment often are caused by activities in another compartment. The nitrate problem in groundwater is a perfect example. Even severe over-fertilisation of agricultural land does create a serious problem for soil quality. Excessive nitrate loads can be quite rapidly removed through the uptake by plants which are subsequently harvested or via leaching. In waters on the other hand, as pointed out before, nitrate is a pollutant of prime concern. Even rather low fractions of the nitrogen fluxes which are turned over in agricultural cropping systems can already cause very serious pollution if they are exported into water bodies. Problems of this kind demonstrate that a holistic, integrative approach is desperately needed. Fig. 2 shows the interconnections between the environmental compartments, animals/cattle, and humans and the pressures arising from pollutant input. The arrows and especially the crosspoints of arrows indicate the problem zones for ecosystem management, which have to be tackled together in an integrative way.
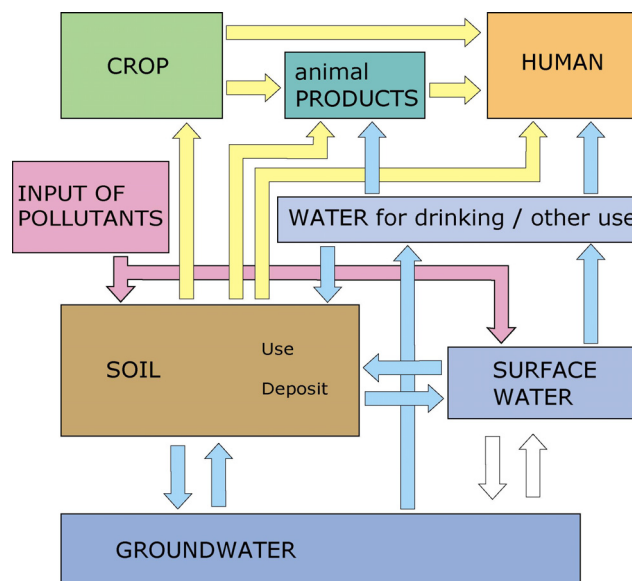
Figure 2: Pollutant fluxes into and out of soil, groundwater and surface water compartments, as well as pathways to human, animal and crop plant receptors.

Expert Statement

Joop Vegter, Technical Soil Protection Committee, The Netherlands
The knowledge about transport, fate and impacts of the most common diffuse pollutants increased significantly during the last decades. Yet there are still many gaps in our knowledge due to the complexity of the soil and water system at various spatial and temporal scales. Moreover, new chemical substances are continuously introduced on the market which may, if adequate controls are lacking, either end up as "emergent pollutants" in the soil and water system or in the upper atmosphere, with potential adverse effects for human health, vulnerable ecosystems or the general life support system of the planet.

The SOWA report states that the quantitative understanding of the soil and water system needed for proper resource management is still generally lacking. This leads to important recommendations for research, which are adequately described in the report, but also for the way we need to frame our environmental policies concerning soil and water. Policies for approval of new chemicals on the market, policies on transport and handling of chemicals and control of the lifecycle of products containing these chemicals, should tighten their preventive controls. Current experiences with the traditional and emerging new diffuse pollution clearly show the need to do this.

Managing the pollution in soil and water is in theory the least preferred option from an environmental protection point of view, but it will remain necessary in view of the imperfection of aforementioned preventive approaches, the intensity of land-use in modern societies and the historical pollution already present in the system. Managing the soil and water system calls for a system-oriented policy approach. An extension of the classical environmental policy model for chemical substances will not do. In the classical model quality standards for chemical substances are derived with scientific methods, the concentration of these substances in the environment is monitored and monitoring results are compared with the standard. If exceeding the standard is likely, legal instruments are put in place to correct the situation and policies are developed for implementation and enforcement. The SOWA report clearly shows that the complexity of the soil and water system and its long reaction times challenges the classical approach. Corrective policies will always be too late. Therefore a proactive management approach is needed, based on the natural scientific understanding of the soil and water system on the one hand and on the other hand the socio-economic understanding of the functions of this system for various land- and water uses. In this resource management model, science is used to develop a strategic policy, which has to be implemented by regional and local management. Quality standards and decision support systems are not goals on their own but tools to assist local management decisions. Monitoring is aimed at the performance of local and regional management.

1   Inventory: Identification of priority compound classes

D. Barcelo, P. Grathwohl, K. Jones, K.-U. Totsche

1.1   Overview

Some of the persistent organic pollutants (POPs) have been deliberately produced by the industry for a wide variety of applications (i.e. pesticides, polychlorinated biphenyls (PCBs), polychlorinated naphthalenes (PCNs). Others are accidentally formed or eventually released as a byproduct from various activities, such as industrial or combustion processes (i.e., polychlorinated dibenzo-*p*-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), polycyclic aromatic hydrocarbons (PAHs). Since 1995, the international community was working on legal instruments to eliminate POPs. Different organisations initiated an assessment process, which in December 2000 resulted in the resolution of the POP Convention. Initial action is taken towards twelve POPs: Aldrin, Chlordane, DDT, Dieldrin, Endrin, Heptachlor, Hexachlorobenzene, Mirex, Toxaphene, PCBs, PCDDs and PCDFs (Tab. 1.1).

Table 1.1: Comparative lists of POPs selected for environmental and toxicological studies.

POPs selected on the Stockholm Convention (2001)	Organic pollutants (or proposed POPs) with an assigned TEF* or REP**	Emerging POPs
Aldrin Chlordane DDT Dieldrin Endrin Heptachlor Hexachlorobenzene Mirex Toxaphene PCBs PCDDs/PCDFs	PCBs PCDDs/PCDFs PCNs PBDEs PBDDs/PBDFs PBBs PAHs	PBDEs PBDDs/PBDFs PBBs

* Toxic Equivalent Factor; ** Relative Potency

Emerging Contaminants (Table 1.2) are suspected of causing adverse effects in humans and wildlife. For instance, pentabromobiphenylether, 4-nonylphenol, C_{10}-C_{13} chloroalkanes and the di(2-ethyl-hexyl)phthalate (DEHP) have been listed as priority hazardous substances in the field of water policy by EC Water Directive 2000/60/EC and the final EU decision No. 2455/2001/EC (Tab. A3.1, Annex). Active hormonal substances (natural hormones are active at levels of ng/l) are being widely used in human and veterinary medicine such as estrogens, anti-inflammatory cortico-steroids and anabolic androgens.

Table 1.2: Emerging compound classes.

Compound class	Examples
Pharmaceuticals	
Veterinary and human antibiotics	Trimethoprim, erytromycine, lincomycin, sulfamethaxozole
Analgesics, anti-inflammatory drugs	Codein, ibuprofene, acetaminophen, acetylsalicilyc acid, diclofenac, fenoprofen
Psychiatric drugs	Diazepam
Lipid regulators	Bezafibrate, clofibric acid, fenofibric acid
β-blockers	Metoprolol, propanolol, timolol
X-ray contrasts	Iopromide, iopamidol, diatrizoate
Steroids and hormones	Estradiol, estrone, estriol, diethylstilbestrol
Personal care products	
Fragrances	Nitro, polycyclic and macrocyclic musks,
Sun-screen agents	Benzophenone, methylbenzylidene camphor
Insect repellents	N,N-diethyltoluamide
Antiseptics	Triclosan, Chlorophene
Surfactants and surfactant metabolites	Alkylphenol ethoxylates, 4-nonylphnol, 4-octylphenol, alkylphenol carboxylates
Flame retardants	Polybrominated diphenyl ethers (PBDEs), Tetrabromo bisphenol A, C_{10}-C_{13} chloroalkanes Tris (2-chloroethyl)phosphate
Industrial additives and agents	Chelating agents (EDTA), aromatic sulfonates,
Gasoline additives	Dialkyl ethers, Methyl-*t*-butyl ether (MTBE)

1.1.1 Persistent organic pollutants

Environmental samples are usually polluted with a variety of compounds and thus represent complex matrices in terms of toxicity assessment. Although soils and sediments may be contaminated with a large number of potentially toxic chemicals, their endpoint-specific toxicity is usually due to only a small portion of these. Valid identification of the portion of toxicants within the mixture directly contributing most to the overall toxicity would therefore greatly help to reduce the pollutant monitoring effort required to track toxicity problems effectively in a rapid and cost-efficient manner.

In the last decades, emphasis has been put on the evaluation of the dioxin toxic potency of different environmental samples. The commonly named dioxin-like compounds (DLCs), such as PCDDs, PCDFs, PCBs and PCNs, were studied in order to determine their relative toxic potency. Recently, some studies indicated that if samples contain both PAHs and DLCs, the PAHs can dominate equivalent estimations. Other emerging contaminants, such as brominated flame retardants, also exhibited dioxin-like activities. The knowledge of the relative contribution of each contaminant to the total dioxin-like activity associated with environmental samples could aid in identifying the most important contributory pollutants (Eljarrat and Barcelo, 2003).

Although consensus values for the relative potencies of the most active PCDDs, PCDFs and PCBs have been established, the database of relative potency values for other DLCs is currently limited (Tab. A3.2, Annex).

The contribution of each contaminant to the total toxicity of environmental samples depends on the relative order of potency along with the contamination levels in the environment. Dioxins are the most potent contaminants. Their levels in soils and sediments, however, are much lower than those presented by other POPs, such as PCBs, PCNs, PBDEs or PAHs. For this reason, greater toxicity contributions of less potent contaminants with higher concentrations could be found. A number of studies have reported PCDD, PCDF and PCB levels from sediments and sludge in North America, Europe and Asia. Regarding the PCB data, a number of studies have reported levels expressed as total PCBs or as a sum of seven indicator PCBs; however, the literature on the dioxin-like PCBs is very scant.

The relative order of potency, along with the wide distribution of PAH, PCN or PBDE contamination in the environment, suggests that monitoring programmes should be extended to include these persistent substances besides the PCDDs, PCDFs and PCBs regularly analysed at present. Quality objectives for TEQs have been formulated in order to assess the quality of freshwater and coastal sediments, resulting in a safe sediment value of 20 pg TEQ/g. Fig. 1.1 shows the concentration levels of each contaminant group needed to reach this safe value. These levels were calculated using the most potent congener of each contaminant group. Moreover, the concentration levels normally found in different sediment samples were depicted. As can be seen, the monitoring of PCDDs, PCDFs and PCBs is important, but other contaminants like PCNs, and esspecially PAHs, need further control (Eljarrat and Barcelo, 2004).

Furthermore, data on brominated dioxin, as well as mixed brominated-chlorinated dioxins are needed in order to determine their environmental impact. However, chemical analysis of mixed halogenated compounds is very difficult in environmental samples due to the large number of possible combinations (there are 4600 potential mixed congeners). In order to achieve this goal it is necessary to develop analytical procedures that permit the determination of different groups of halogenated contaminants.
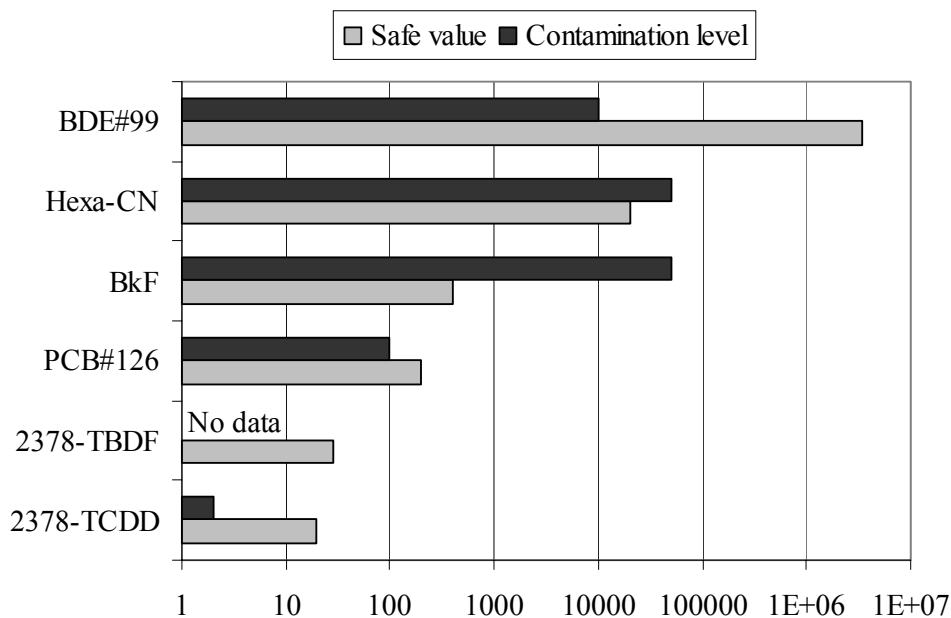
Figure 1.1: Comparison between safe concentration levels in sediments and concentration levels generally found in sediment samples (values expressed in pg/g).

1.1.2   Emerging contaminants

Surface water contaminated by municipal and industrial sources, and diffuse pollution sources from urban and agricultural areas continue to build up pollution levels in the environment. Numerous field studies, designed to provide basic scientific information related to the occurrence and potential transport of contaminants in the environment are being continuously conducted with the aim to identify which contaminants enter the environment, at what concentrations, and in what combinations. A large body of literature exists on occurrence of specific groups of organic contaminants in the environment. However, in the past research priorities have focused on priority pollutants, such as POPs, pesticides, toxic metals, radionuclides. Only recently, the attention of the scientific community has started to shift to emerging contaminants. Therefore, a major challenge will be to identify the chemicals which potentially will become dangerous in the future. It has to be cleared if it is sufficient to look (just) for persistent, high flux, toxic, endocrine active compounds.

The major sources of environmentally relevant emerging contaminants are primarily wastewater treatment plants effluents, and secondarily terrestrial run-offs (roofs, pavement, roads, agricultural

land) including atmospheric deposition. Characteristic of some contaminants is that they do not need to be persistent in the environment to cause negative effects since their high transformation/removal rate is compensated by their continuous introduction into the environment. For most of the occurring emerging contaminants, risk assessment and ecotoxicological data are not available and therefore it is difficult to predict which health effects they may have on humans, terrestrial and aquatic organisms, and ecosystems. Also the budgets (sources, entry routes, and fate) for environmental pollutants would be of importance. Tab. 1.3 summarises the data regarding the occurrence of several emerging contaminants in the environment.

1.2   State-of-the-art and research gaps / solution strategies

1.2.1   Sewage sludge used in agriculture as a source of diffuse pollution of soils

Wide-spread-custom in Europe is the application of sewage sludge on agricultural land. With the implementation of the 91/271/EEC Directive on urban wastewater treatment, more than 40.000 sewage treatment plants will be needed in Europe till the year 2005. It has been estimated that the amount of sludge produced in Europe will increase from 6.5 to 11 millions tonnes in the year 2005. At present around 40 % of the sewage sludge produced in Europe is deposited in landfills and 40 % goes to agricultural land, whereas the rest is directed to incineration and below 10% still is dumped to the sea. According to the EU the quantity of sludge re-used would represent around 53% of the total sludge produced. In general, the EU considers that the re-use of sludge should be encouraged since it represents a long-term solution provided that the quality of the sludge re-used is compatible with public health and environmental protection requirements. A soil protection policy document has been recently released by the European Union e.g. as defined recently by DG ENV (*Towards a Thematic Strategy for Soil Protection*, COM(2002), 179 final) and the EC (IP/02/592; 19/04/2002) that points out the problems associated with soil protection, including soil amendment with sewage sludge. Many of the organic contaminants that are released from the sludge used for agriculture are not currently regulated. However, for the new directive[1] limit values for several organic pollutants in sludge added to agricultural soil are being discussed (Fig. 1.2; Petrovic et al., 2001). In some member states incineration of sewage sludge is discussed as the more ecological alternative to application on agricultural soils.
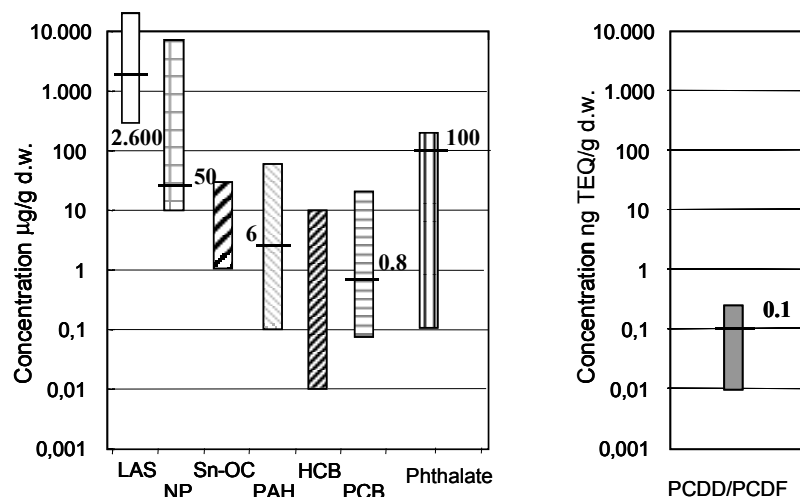
Figure 1.2: Levels of anthropogenic chemicals in sewage sludge and limit values for sludge to be applied onto soil (European Commission, 2000 draft proposal)

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[1] Working Document on Sludge, 3rd Draft, 2000, unpublished

Table 1.3: Summary data for selected emerging contaminants.

Compound	Origin	Persistence Bioaccumulation	Observed in the environment	Concentration level
Nonylphenol	Degradation product of non ionic surfactants	Medium persistent/ bioaccumulative	Soil Sediment Sludge Water	Low mg/kg* Low mg/kg Low-high mg/kg Low µg/L
Bisphenol A	Plastics	Not bioaccumulative	Surface water Groundwater	Low-high ng/L Low-high ng/L
Phthalates	Plastics	Low to medium persistent atmospheric deposition	Water Sediment Sludge	Low-medium µg/L Low µg/kg Low-medium µg/kg
PBDE	Flame retardant	Persistent/highly accumulative atmospheric deposition	Sediment Soil Sludge	Low-medium µg/kg Low-high ng/kg* Low-medium µg/kg
C_{10}-C_{13} chloroalkanes	Flame retardant	Persistent/ bioaccumulative	Surface water	Low-medium µg/L
Sulphonamides	Human and veterinary drug	Slightly-very persistent	Groundwater	
Tetracyclines	Human and veterinary drug	Moderately-very persistent	Groundwater Soil Sludge	
Steroid sex hormones	Contraceptives	Moderately persistent	Water Sediment Sludge	Low ng/L Low µg/kg Low-medium µg/kg
MTBE	Gasoline additive	Persistent/ not bioaccumulative - but ubiquitous in the atmosphere	Groundwater	

*sludge amended soil

1.2.2   Future research tasks

A still increasing number of organic chemicals is being introduced to the market and thus released to the environment. Based on a single species risk and fate assessment, we will be unable to screen all these chemicals for their potential environmental and human hazard, as we have done for example for selected POPs, heavy metals and pesticides. New approaches have to be found and developed to estimate the human- and ecotoxicological risk as well as the environmental fate of whole groups of substances on the base of the structure and molecular properties.

The following research needs concerning the assessment of water/soil systems were identified (coming from several EU funded projects from the 5th and 6th Framework Programme in "Water cycle, including soil related aspects", subpriority Global Change and Ecosystems in the Environment and Sustainable Development):

1.   There is an urgent need for a European list of emerging contaminants, as possible candidates for the introduction into the WFD list of priority substances. This list is amendable for revision and addition of new contaminants each four years and thus, based on surveys and on the results of further monitoring programs the lists of new pollutants could be integrated. To achieve this, a systematic survey of emerging contaminants in waterways should be undertaken. An example at

the EU level of such systematic survey corresponds to the EU Project Removal of Persistent Polar Pollutants through improved treatment of wastewater effluents P-THREE (EVK1-CT-2002-00116), where such systematic survey at different EU countries takes place and it will be available shortly. The resulting combined list of priority and emerging pollutants will represent an initial step towards a more detailed picture of environmental contamination and better understanding of soil-water-sediment functioning beyond priority pollution. Further features can be added: concentrations/frequency of occurrence, physico-chemical, environmental and ecotoxicological properties of the compounds...

2. The interaction of chemicals between soil and water is a key issue. It is expected that the chemical composition (geochemical and man-made pollution) of the soil and the biological and chemical processes will determine the resulting water quality. An important aspects to be addressed is the mobility of contaminants within sediments and soils and their bioavailability and pore water concentrations. Research needs in the specific area of sediments are being addressed by the European Sediment Research Network (SEDNET) EC contract No. EVK1-CT-2001-20002. The executive summaries of the different workshops provide selected items that can be explored furtheron in future RTD projects.

3. A further source of diffuse contamination are compost materials/organic waste containing heavy metals and emerging organic pollutants. Further research has to address mass balance concepts for the input/output of heavy metals and organic compounds into compost materials and from these materials into soil and water. Concepts of quality definitions have to developed.

4. There is a lack of studies to assess the functioning of the water-soil system such as investigations on the behavior of emerging contaminants in surface water and groundwater during artificial recharge. In this way the river bank can serve as an attenuation barrier for groundwater pollution. A better understanding of contaminant transport and fate of emerging pollutants is a key issue for an efficient design, operation and optimization of bank filtration that will reduce the amount of treatment needed at drinking water treatment plants.

5. Typical concentration levels in environmental matrices such as soil, water and sediments have to be monitored in dedicated long-term monitoring sites in order to allow an early recognition towards increasing concentrations and deteriorating trends in specific soil functions (such as the filter and buffer capacity).

Most relevant scientific questions

1   Inventory: Identification of priority compound classes such as persistent organic pollutants and heavy metals (= WG1)

- What are the **ways to identify chemicals which potentially are dangerous in the future**? Is it sufficient to look for persistent, high flux, toxic/endocrine active compounds? How can dilution effects (concentration vs. volume) be included?

- Can the **effects and risks of anthropogenic compounds** (and compound mixtures) **on organisms and ecosystems** be predicted?

- What are the **budgets for environmental pollutants** depending on the scale of observation (identify and quantify various sources; route of entry and fate of pollutants into/in the environment, accumulation and degradation, monitoring)?

2   Biogeochemical and physical processes

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2.1   Overview

Contaminants dissolved in the soil solution migrate by three basic mechanisms: advection, molecular diffusion and mechanical dispersion. From the macroscopic point of view, the process of advection is fully determined by the soil water velocity field. The processes of molecular diffusion and mechanical dispersion are usually described using identical physical means (Fick's law) and can therefore conceptually be combined into a single process – hydrodynamic dispersion. Migration, however, is not limited to the dissolved phase. Contaminants may attach to colloidal or suspended particles. Once mobilised, these particles can carry even strongly sorbing organic and inorganic contaminants. While the fundamental physics and chemistry of colloid and carrier affected transport is understood, the relevance for contaminant spreading and transport is still not known. Especially the environmental conditions and porous media properties which favour the formation, mobilisation and transport of inorganic and organic colloids are essentially unknown. As the conditions for the retardation and immobilisation have to be clarified as well, no valid and reliable assessment of the risk exposed by carrier affected transport is possible.

Contaminants migrating through the soil are reacting with the soil constituents and undergo complex physical, chemical and biological transformations. Most contaminant transport mechanisms in soils are mediated or at least strongly affected by the presence and movement of soil water. Thus, deep knowledge on the physics and chemistry of soil water movement in heterogeneous and dynamic systems is an essential prerequisite for a valid and reliable estimation of the contaminant fate. This, of course, requires our lasting efforts to gain a better understanding of the movement of water in heterogeneous porous media.

Under natural conditions, macroscopic soil properties often vary considerably in both space and time. Since these properties change from point to point at multiple scales, the heterogeneity and spatial variability needs to be conceptualised as a hierarchical system (see chapter 3). Another source of complexity is related to the natural soil water and soil air regime. The soil surface is exposed to continually changing radiation fluxes, reflected in evaporation changes and surface temperature gradients. The supply of water to the surface in a form of precipitation is highly irregular in time and space. There are complex interactions between plant roots, rhizosphere micro-organisms, and soil constituents. Vadose zone processes are strongly linked to groundwater recharge quantity and quality.

After entering the soil, contaminants may dissolve/disperse in soil water, attach to mobile and immobile soil particles, partition to soil air, or even form separate non-aqueous phase liquids (NAPLs). Despite the fact that numerous research projects in the past focussed on the understanding of the contaminant fate in soil and aquifer systems, we still lack in deep knowledge on how soils process contaminant inputs under natural, i.e., environmental conditions in the long run. In particular, long term effects which result in aging phenomena are known to play a prominent role in the attenuation of contaminants. It is, however, essentially unknown which mechanisms contribute to aging and which properties favour such phenomena.

An essential question of the fate of contaminants in soils is the affect of the structural and functional biodiversity. While numerous studies have proved the effect of microbial populations on the persistence of contaminants at the bench scale (microcosm and biodegradation studies), the interdependence of long-term contaminant inputs in soils with soil flora and fauna and vice versa is essentially unclear. One reason is our principle knowledge gap on the functional biodiversity. Up to now, studies aiming at biodiversity mainly concentrated in the assessment of the structural biodiversity. How soil flora and fauna functioning affects contaminant fate and turnover rates and how contaminants affect the functioning of the subsurface microbial community is a key issue of future soil research.

Due to the complexity of the processes determining the transport of contaminants in soils, it seems to be practically impossible to formulate a completely unified quantitative description of the phenomena, which would adequately explain processes at all involved time and space scales. Instead, specific methodologies are used to solve predefined classes of problems. On the other hand unifying views are necessary when complex large scale contamination problems are to be solved.

2.2   State-of-the-art and research gaps / solution strategies

2.2.1   Physical processes

2.2.1.1 Determination of soil hydraulic properties

The predictive strength of models to simulate variably saturated flow and transport in soils is often seriously affected by inadequate description of the involved soil hydraulic properties, i.e. the water retention curve and unsaturated hydraulic conductivity function $K(h)$. Inadequate description of soil hydraulic properties can be partly attributed to problems associated with the validity of the Richards equation at the transition between saturated and unsaturated zones (i.e. the soil / groundwater interface), and partly to difficulties involved in experimental and data processing procedures used when the hydraulic functions are evaluated. Several indirect methods for $K(h)$ determination, mostly based on capillary models of porous media and laminar pore flow assumption, are available. In the frame of these methods, the relative unsaturated hydraulic conductivity $K_r(h)$ is predicted from the more easily measurable water retention curve $\theta(h)$, closely associated with the statistical pore size distribution function, while the saturated value of the hydraulic conductivity, K_s, is determined experimentally.

Most of the soil hydraulic methods incorporate coupling of the retention and conductivity functions through a $K_r(h)$ predictive formula, thus adopting some features of the indirect methods. The complete uncoupling of the two hydraulic characteristics is in principle possible, but in practice almost never used. A partial uncoupling can be achieved by dissociating some of the $K(h)$ parameters from their $\theta(h)$ counterparts. An example of such a parameter is the exponent of the tortuosity factor in the $K_r(h)$ function. In a way, the saturated conductivity, K_s, can also be interpreted as an "uncoupled" parameter of $K(h)$.

Although widely recognised in its relevance, the problem of determination of soil hydraulic properties for the flow and transport modeling purposes is still not resolved. As most of the transport processes in soils are mediated or affected by soil water, knowledge on the physics and chemistry of soil water movement in heterogeneous and dynamic systems is essential. This classifies the topic of soil water movement as a lasting and still highly relevant research goal for the future.

2.2.1.2 Inverse modeling of coefficient functions and parameters of soil properties

By definition, the unsaturated hydraulic conductivity $K(h)$, as a proportionality factor in the Darcy-Buckingham law, is equal to the fraction of the volumetric flux and the hydraulic gradient. When evaluating this fraction for a certain value of pressure head h one solves a simple inverse problem for Darcy's equation. While this is sufficient for steady state flow, the inversion of Richards equation is needed for transient flow conditions. Steady state is often very difficult to establish experimentally for unsaturated flow. Fortunately, due to the much-improved availability of the computer-aided numerical simulation techniques, the inverse solution of the full Richards equation for general initial and boundary conditions is now possible. In this context the term inverse modeling is often used to denote the methodological framework that has developed around the solution of the inverse problem for flow and transport governing equations.

Basic hydraulic parameters of soil water flow

The *permeability* k (m^2) of a porous medium can be estimated from soil structure properties. Such relationship is offered e.g. by so called Kozeny-Carman formula:

$$k = C_0 \frac{n^3}{(1-n)^2 M_s^2}$$

where n is the porosity, M_s is the specific surface area of the solid matrix (defined per unit volume of solid), and C_0 is a coefficient for which Carman suggested the value of 1/5.

The relationship between soil water flux and hydraulic gradient is described by Darcy's law:

$$q = K \frac{\Delta H}{\Delta L}$$

in which the proportionality factor K (m/s) is called *hydraulic conductivity* ($K = gk/\nu$, where g is the acceleration of gravity and ν is the kinematic viscosity of water). The head drop per unit distance in the direction of flow is the hydraulic gradient ($\Delta H/\Delta L$), and the volume of water flowing through a unit cross-sectional area per unit time is the soil water flux (q). The Darcy's law is often referred to as Darcy-Buckingham law when related to unsaturated flow, in which case the hydraulic conductivity is a function of soil water content and is called *unsaturated hydraulic conductivity*. At saturation, the unsaturated conductivity is equal to saturated hydraulic conductivity (usually denoted as K_s), which is identical to the Darcy's K.

Under unsaturated conditions, water is held in soil pores mainly by capillary forces. The magnitude of these forces is expressed by Laplace equation:

$$p_c = \frac{2\sigma}{r}$$

where p_c is the capillary pressure (Pa), σ (N/m) is the surface tension (air-water interfacial tension) and r (m) the effective radius of curvature of the air-water interface (formed by capillary menisci). The capillary pressure strongly depends on soil water content. The functional relationship between the two quantities is called *retention curve*. In this function, the capillary pressure is often converted to the units of water head and denoted as capillary pressure head (h_c) or pressure head (h).

Basic hydraulic parameters of the conservative solute transport in soils

The *coefficient of hydrodynamic dispersion* consists of two components (reflecting two different dispersion mechanisms: molecular diffusion and mechanical dispersion). For one-dimensional solute transport in variably saturated soil, the dispersion coefficient is usually considered to be of the form

$$D = \tau D_o + \alpha v$$

where D_o is the *coefficient of molecular diffusion* in free water (m^2/s), α is the *dispersivity* (m), τ is a *tortuosity factor* (τ varies with changing soil water content), and $v = q/\theta$ is the soil water velocity (m/s). The dispersivity is soil specific hydraulic parameter, which characterizes mechanical dispersion. The process of molecular diffusion is described by Fick's law, which expresses the solute movement due to concentration gradient

$$J = -D_o \nabla c$$

here J is the mass flux of solute (kg m^{-2} s^{-1}) and c is the solute concentration (kg/m^3).

In general, inverse methods for identifying relevant coefficient functions and parameters of all different kinds of processes in soil gain more and more relevance. Inverse methods can be used to identify rate parameters of elimination reactions, coefficient functions for contaminant retardation and much more. A particular application of inverse methods is the discrimination between competing process parameterisations. The important open research problem is the formulation of appropriate objective functions and the formulation of quantitative criteria which allow to uniquely and clearly determine a model with the highest predictive value. Nevertheless, when this technique is used to identify either soil hydraulic properties or coefficient function and properties of biological and chemical processes in soil from observed time-space variations of more easily measurable state variables, the proper choice of a limited number of parameters has to be made to represent the respective functions in an optimisation algorithm. The fewer parameters there are, the more effective the parameter optimisation process. This feature again favours the use of more simple parameterisations of the relevant processes. In addition, many problems related to computational efficiency, numerical convergency and uniqueness of the inverse modeling approach remain to be solved.

2.2.1.3 Sampling resolution vs. process resolution

As for most geo- and hydrological sciences, nearly all data acquisition is done at a small scale. However, most processes that are of practical relevance are at the pedon or larger scale. Connecting scientific understanding between point measurements and e.g. ecological scales is not possible with the available approaches. For making this connection, more research is certainly required (see 4).

2.2.1.4 Soil-plant-atmosphere interactions

Large gaps exist in our knowledge and understanding of soil-plant-atmosphere interactions at the ecosystem level such as soil-vegetation-atmosphere interactions or hierarchical and dynamic root systems. However, as the relationship between ecosystem research aspects (often biotic) and abiotic research aspects is still not quite close, a major exchange of approaches is needed.

Flow and transport processes taking place at the soil surface and within the upper soil layers, which accommodate the plant roots, are subject of interest for a number of disciplines of natural, technical and agricultural sciences, among others meteorology, soil hydrology and plant physiology,. Many advances have been achieved in describing the processes both qualitatively and quantitatively in the frame of each of these disciplines, however, very often the resulting approaches tend to be biased and many important processes oversimplified, due to the limited scope of view of the individual discipline. Consequently, there is an urgent need for much closer cooperation between the researchers representing different fields of science to come up with new interdisciplinary solutions, so that more complex real world problems can be addressed. Following are selected examples of the 'interdisciplinary' research gaps which may have serious impact on transport of contaminants in soils.

- Basic soil hydraulic properties (such as retention curves and hydraulic conductivities) are routinely measured for soil layers identified by regular soil surveying. However, very little attention is usually paid to the properties of the first several centimeters of soil near the soil surface. In soils fully covered with vegetation, this thin layer is very different from the average topsoil material. Often the standard measurement techniques are useless because of the unstable nature of the soil organic matter. New/existing methods for assessing the near surface hydraulic properties need to be developed/improved and brought to common use. A little bit more is known about the soil crusting for soils without plant cover (e.g. during the spring time in arable lands), however, little of this knowledge has been transferred into standardised experimental methodologies.

- The origin and development of a root system in soils is a complex and yet scarcely understood subsurface phenomena. At present, we are not even able to quantitatively describe static root systems more complex than those developed by single species grown in a pot. We know, of course, that roots interact with the solid phase in manifold mechanical, physical and chemical

ways to accelerate weathering and increase nutrient availability. We understand that soil structure and pore system morphology together with other properties determines direction of root growth and root system development. How these physical and biological processes and properties work together resulting in complex structured hierarchical and dynamic root systems, and how such systems interact and communicate with the biotic and abiotic environment, is "terra incognita". Its knowledge, however, is of fundamental importance for the understanding of contaminant fate in the highly active and dynamic rhizosphere and such is a challenge to an interdisciplinary research.

- Ecologically, the effect of soil water flow and retention is important for the availability of water for crops and vegetation. This availability is known to be spatiotemporal variable, and this renders root water extraction spatiotemporal variable. For schematised situations, these dependencies have been addressed, but nevertheless, to relate the type of vegetation quantitatively to the soil water regime with a mechanistic basis is now an emerging field of research.

- During the past few years, the relationship between vegetation and soil water regime has been addressed mainly for water-stressed (semi-arid) conditions and it has been found that the various feed back mechanisms may lead to 'self organisation' of vegetation patterns. For temperate regions, water availability is not likely to control which vegetation develops, and other growth factors may have to be taken into account, such as the nutrient element status. At this moment, it is impossible to predict vegetations and vegetation sequences as a function of time in dependence of water regime and other growth factors. At best, correlative approaches relate vegetations and growth factors.

- Geochemical and biological processes are predominant factors of the fate and transport of contaminants in soils and the unsaturated zone. Detailed modelling approaches have been developed to describe their occurrence and effects. But, in each case the developments are limited in their application due to a lack of precise knowledge and validated concepts for the coupling of those processes with complex water transferring systems. To overcome this gap, more inter-disciplinary modeling approaches must be proposed, following a step by step experimental identification and validation of mechanisms models and especially coupling concepts. The development, test and validation of such coupled modelling for simulating the fate and transport of contaminants in soil and unsaturated zone systems is an emerging fundamental challenge in environmental sciences.

2.2.1.5 Preferential flow and preferential transport

Structured soils contain a highly-permeable macropore or fracture pore system through which water and solutes can move at considerably higher velocities than in the porous matrix. Consequently, local (sub-macroscopic) non-equilibrium conditions in the transient pressure head and solute concentration may develop. Such preferential flow phenomena severely limit the prediction of water and solute movement. Preferential flow related to soil structure has been widely reported in soils containing wormholes, root channels, and inter-aggregate fissures. Additional types of preferential flow have been linked to textural differences rather than structural effects. Two types of preferential flow phenomena, that belong to this category, are fingering and funnelled flow. The evolution of finger-type preferential flow paths is associated with gravity-driven flow instability. Fingering occurs in water repellent soils, when water percolates from a fine-textured into a coarse-textured layer, or when the air pressure increases ahead of infiltration front. To what depth preferential flow takes place is largely unknown and depends much on subsurface heterogeneity.

Most field soils exhibit different types of spatial heterogeneity, such as soil spatial variability and soil structure, which often coexist. When quantitative description of soil water flow is based on the traditional continuum approach, the notion of spatial variability relates to spatial distribution of macroscopic model parameters, such as hydraulic conductivity. However, in soils with strongly developed structure, microscale effects sometimes become so dominant that they affect macroscopic flow and transport processes. Both spatial variability in soil hydraulic properties and structure-induced hetero-

geneity can contribute to the initiation of preferential pathways. The challenge is to adequately account for both types of spatial heterogeneity.

Small-scale heterogeneities related to soil structure can be modeled either by using a discrete fracture network model or a multi-continuum approach. Within the discrete fracture network concept, a map of the structural geometry must be known, while with the multi-continuum approach two or more continua, representing matrix and fracture systems, share the same space domain.

Heterogeneity in continuum models can be modeled using both single- and dual-porosity/permeability approaches. Single-porosity models assume that preferential pathways may develop as a result of spatially-variable soil hydraulic properties. Spatially distributed soil hydraulic properties, for example generated deterministically or as random functions of the spatial coordinates, lead to characteristic patterns of relatively low and high flow velocities within the flow domain. In this case, local equilibrium is preserved.

The dual-porosity/permeability approach, on the other hand, assumes that the porous medium consists of two domains with different hydraulic and transport properties. The term dual-permeability is used to indicate that flow takes place in both domains in contrast to dual-porosity approach, which is often used in the context of mobile-immobile-type solute transport modeling. Water flow and solute transport in dual-permeability models are described using separate flow and transport equations for the fracture and matrix pore systems. Crucial components of these types of models are transfer terms governing the exchange of water and/or solutes between the fracture and matrix pore systems. Empirical and semi-empirical expressions exist that are applicable to transient unsaturated flow, however, more research is needed to establish more adequate and computationally feasible relationships and to develop experimental methodologies needed to determine the additional constitutive parameters for dual-porosity/permeability models.

2.2.1.6 Multiphase flow

Experimental and computational techniques currently used for determination of soil hydraulic and transport properties are often inadequate for solution of many practical field scale problems of water flow and contaminant transport. Regarding flow, significant advances have been made conceptually, numerically (including software tool development), and by analytical studies. Nevertheless, for a particular type of flow problems, i.e., the multiphase flow of water, gas, and NAPLs, models have been developed only during the last decade and the scenarios that have been studied are still relatively scarce and simplified. Consequently, well based predictions on the basis of a well developed understanding and theory are still left for the future. For instance, the rate of lateral spreading of floating LNAPL lenses at the groundwater table have been mainly considered for rather homogeneous situations (both numerically and analytically). Also the spreading of NAPLs above coarse/fine (and vice versa) layer interfaces has been studied, but only for relatively simple boundary conditions (homogeneous layers). Hence, one of the main problems, the volume of soil and aquifer contaminated by erratic flow of DNAPLs, in realistically layered non-homogeneous porous medium, cannot be assessed. For similar reasons, the dissolution of free liquid into the aqueous phase, as well as the volatilisation of important NAPLs to the soil atmosphere, and the concentration levels and time periods involved, are still practical questions to which current science cannot provide a reasonably accurate answer. Recently, studies of multiphase flow by Wipfler et al. (2004) and Marsman (2002) revealed that it is possible to predict LNAPL spreading in layered porous media. However, it appeared not well possible to predict such spreading in case of fluctuating groundwater tables. Omitting details, it is remarkable that the cause for the latter observation was believed to be the poor applicability of the soil hydraulic functions (conductivity and retention functions), which were fitted to the same system as for which the spreading process was studied. The implication is that the common ways to parameterize the soil hydraulic functions is too insensitive for allowing the simulation and prediction of more complex flow problems.

2.2.2 Biogeochemical processes

2.2.2.1 Biogeochemical interactions

Geochemical and biological processes are predominant factors of the fate and transport of contaminants in soils and the unsaturated zone. Often these processes are studied separately. Detailed modeling approaches have been developed to couple the description of water flow and geochemical interactions. In parallel, attempts have been performed to couple the description of microbiological activities with geochemical interactions. They are functionally strongly related, where small scale heterogeneity serves as an important factor to provide a niche for surviving organisms, a starting point for colonising other parts of the soil, and where an adequate linkage of biotic and abiotic factors is necessary for the assessment of the response of the ecosystem to contamination, the ability to buffer and transform pollutants, and of the integrity of the soil ecosystem/food chain. In addition to the understanding and modelling of biogeochemical interactions, it is necessary to predict the impact of these coupled processes at transient flow conditions in the unsaturated zone. The complexity of these coupling phenomena is one of the major barriers for practical application of the present knowledge in each discipline (e.g. soil physics, geochemistry, plant physiology and microbiology). To overcome this gap, more interdisciplinary modelling approaches must be proposed, following a step by step experimental identification and validation of the model modules. The development, test, and validation of such coupled models for simulating the fate and transport of contaminants in soil and the unsaturated zone is an important task in the environmental sciences.

Besides the conceptual and parameterisation problems, the numerical demands may also be recognised as being considerable for such complex systems. In recent work (Schröder et al., 2004), heavy metal behaviour in Dutch river flood plains was studied in its dependency of groundwater table fluctuations and periodic flooding. Predictive adsorption models were for this purpose combined with dissolution/precipitation reactions, taking redox potential and pH-variations into account. Despite that a relatively flexible object oriented code was employed (ORCHESTRA), it took great effort to obtain numerical solutions, whereas other proven codes, that are used worldwide, were not robust enough for reaching convergence. This observation indicates that the combination of current soil chemical models, that take into account the more complex adsorption models (Nica-Donnan, Wham) as well as a range of solid phases that are subject to dissolution and precipitation reactions, with transport algorithms, may be beyond our current reach.

2.2.2.2 Structural and functional biodiversity

Another, yet still neglected aspect of the biogeochemical interactions in soil is the mutual interdependence of long-term contaminant input and the presence and the structural and functional biodiversity of soils and aquifers. While the principal role of the subsurface community for the contaminant fate is obvious (degradation, mineralisation, metabolisation, humification, immobilisation and formation of bound residues), we essentially lack the knowledge with respect to the effect of contaminants on the microbial community and its activity. Thus, neither the formation of metabolites nor the export of contaminants, metabolites and degradation production nor the development of contaminant turnover rates can be estimated à priori. Thus, our current understanding of natural attenuation is based on assumptions that the present biological activity as well as the environmental boundary conditions stay constant over time. With this, however, it is intrinsically presumed that the active microbial community at a site und thus the functional diversity is not affected by the contaminants. This assumption, besides most other assumptions on the biodiversity in soils, is completely unproven. The most prominent reason for this fact, of course, is our principle knowledge gap both with respect to the functional biodiversity and the structural biodiversity in soils. The few studies on soil biodiversity worldwide conducted up to know aimed at the assessment of the structural biodiversity, while the aspect of functional biodiversity is a key issue within the biodiversity research in general.

During the past decade, it has become more explicitly realised that the soil foodweb is quite complex. Moreover, it has been established that the fraction of biomass associated with different organisms is not an appropriate parameter with regard to the importance of such organisms in the soil foodweb: organisms that are not numerous may in fact be more vital for the entire foodweb. Unfortunately, it is

not known how the soil foodweb responds to changes in environmental conditions, and this is a major gap in knowledge if one aims to predict the results of climate and land use change on soil systems.

The functioning of the soil microbial community with respect to contaminant turnover rates on one hand, and the effect of the long-term exposure of the soil microbial communities to high levels of contamination and frequently complex contaminant mixtures must therefore become a key topic of future soil research.

2.2.2.3 Sorption of heavy metals

Heavy metals and other toxic elements are subject to a complex geochemical speciation in the unsaturated zone. Thermodynamic data of the main part of inorganic water/mineral reactions are with respect to pure minerals. Additionally, the conceptual approach of interface interactions between solid compounds (including complex minerals and natural organic matter) is well developed. It includes the description of ionic exchanges on charged interfaces, surface complexation, and co-precipitation in specific mineral solid solutions. But the validation of the different concepts and the quantification of related parameters are still uncertain and subject to scientific discussion. The state-of-the art for the interactions between solutes and organic ligands or organo-mineral colloids is approximately at the same level. As a consequence of this fragmented knowledge, detailed geochemical codes are available for scientists using precise thermodynamical data of equilibrium systems, but the uncertainty concerning the reaction kinetics is an important obstacle for understanding and hence modelling of real world fate and transport of toxic elements even in quite simple and well-controlled lab-conditions. For some heavy metals or other toxic elements, the speciation can be extended to organo-mineral geochemistry. In this case, some chemical species are known and their behavior is more complex due to potential volatilisation and biotransformation (for example Hg, Sn, As).

If the thermodynamical equilibrium constraints are in many situations well known, the occurrence and determination of kinetic limitations is a gap to be filled by scientists. As a matter of fact, many types of kinetic limitations can occur in natural systems and the state of speciation is sometimes completely out of the equilibrium domain. Close to the equilibrium, concepts are available to model kinetics limitation on a thermodynamical basis. However, in many cases, scientists have to deal with mass transfer limitations linked to molecular diffusion in heterogeneous porous media or to biologically driven kinetics (e.g. in the case of oxydo-reduction processes in soils) which superpose to other coupling effects due to dispersion in porous media.

The modelling approach needs to be developed on experiments and measurements. Thus, the experimental study of heavy metals and other toxic elements is fundamental prior to modelling. The analysis of total content of inorganic elements in soil, underground or sediment samples is not sufficient. Even the use of selective or sequential extraction of those elements from samples is difficult to interpret the results in terms of *in situ* speciation. Consequently, there is an urgent need of innovative methods for the determination of the speciation of elements in heterogeneous samples. These methods must be developed through a close cooperation between analytical chemists , biogeochemists and soil scientists. As Schröder et al. (2004) and others showed, it is possible to predict (i.e., not fit) heavy metal adsorption with current generic models such as the Nica Donnan model. What is more important, though, is that this is possible only for some heavy metals (pure prediction with accuracy of a factor of about two for Cu, Cd), as for Pb and Zn important discrepancies remained between model and data, that could not be removed in a consistent way. Why these metals still escape a better prediction, is unknown at the moment.

Microbiological processes are known to be key steps in the dynamics of some major environmental elements (e.g. H, Fe, S, C,...). Thus, these processes will interact with all elements depending on mineral species linked to microbiological activities (iron oxy-hydroxides, sulfides and sulfate, pH and Eh variations, carbonate and dissolved organic carbon contents,...). The description of these coupled processes need an interdisciplinary approach involving geochemists, microbiologists and numerical model developers.

2.2.2.4 Interactions and metabolisation of organic pollutants

Organic pollutants are also subject to complex interactions in soils. The main difficulty is the potential biotransformation of these compounds and the limitation of the bioavailability of these compounds due to physico-chemical interactions with organic matter and other reactive soil components. The consequence of biological transformations is the occurrence of many metabolites before the hypothetic complete mineralization of contaminants. These metabolites will be characterised by different toxic properties, different fate and transport patterns, and by potential interactions with the original contaminants. This "speciation" of organic contaminants is related to biochemistry and microbiology. The more classical concept for describing organic interactions in soils is based on linear partitioning between organic matter and the aqueous solution, and linear kinetic biodegradation. In many real field situations, this concept is not sufficient. Linear partitioning is only justified if unsoluble and soluble organic matter remains constant quantitatively and qualitatively during the fate and transport of the organic pollutant. Linear kinetic biodegration is only justified for an apparent one-step biodegradation, independent to other biological processes. The presence of solutes modifying the solvent properties of the aqueous phase (e.g. more or less polar solutes), the modification of the physical state of the unsoluble organic matter (e.g. solid-liquid transitions depending on temperature), and the complexity of micro-organism community metabolisms induce generally non-linear behavior which must be taken into account to model systems.

The occurrence and determination of kinetic limitations is also a gap to be filled by scientists in the case of organic pollutants. Scientists have also to deal with mass transfer limitations linked to molecular diffusion in heterogeneous porous media (for example diffusion in the organic matter matrix) or to biologically driven kinetics which superpose to other coupling effects due to dispersion.

Microbiological processes are known to be influenced by many physical (water content, temperature, ...) or inorganic chemical limiting factors (oxygene, nitrogen, pH, toxic elements, ...). Thus, these processes will interact with all interacting mineral species, needing again an interdisciplinary solution involving geochemists, microbiologists and model developers.

2.2.2.5 Role of mobile sorbents (organic and inorganic)

Mobile sorbents such as dissolved, colloidal phase and suspended inorganic and organic particles affect flow of water and transport of solutes in soils. Major processes between the solution and the solid phase, such as sorption, partitioning, speciation and ion-exchange are influenced by the interactions with mobile sorbents. Their presence affects the solubility of solutes due to complexation, solubilisation, carrier association and the solvophobic effect. In recent years, research has focused on processes leading to mobility enhancement of organic and inorganic pollutants. The issue was to understand to what extent mobile sorbents may facilitate contaminant transport in porous media with respect to risk assessment, soil and groundwater reclamation and clean-up. Major compounds which have been shown to increase the solubility and thus the mobility of nutrients and contaminants are surfactants, co-solvents, (hydr)oxides, clay and other minerals, humic substances and humin-coated inorganic colloids. In contrast to aquatic environments, the major amount of dissolved and colloidal-sized constituents in soils is either biotic or organic in nature or composed of inorganic matter with organic coatings. Due to their chemical properties, i.e. the high concentration of functional groups and the chemical diversity, these substances interact with the immobile solid phase as well as with other dissolved and colloidal phase components in the liquid phase. Contaminant facilitated transport in the presence of mobile sorbents applies to such environmental conditions where these substances have to be considered non-reactive, i.e., neither filtration nor sorption or partitioning to the immobile solid phase occurs. In soils, however, mobile sorbents have to be considered reactive and are subject to immobilisation due to interactions with the immobile solid phase. In such environments, the retention of mobile sorbents may cause reduced overall contaminant mobility due to immobilisation. The underlying process has been described as co-sorption. Sorption of mobile organic substances can as well lead to an increase of the organic carbon content of the bulk soil, thus increasing the number of potential contaminant binding sites, a process, described as cumulative sorption.

While the fundamental physics and chemistry of colloid and carrier affected transport is understood, its relevance for contaminant spreading is essentially not known. In particular, understanding of the environmental conditions and porous media properties which favour the formation, mobilisation and transport on one hand and the retardation and immobilisation on the other hand is needed. Moreover, the effect of mobile sorbents on the mobility of contaminants under changing environmental settings has to be addressed in future research. One objective is to define qualitative and quantitative criteria to distinguish between the effects on contaminant mobility that derive from processes which lead to mobile sorbent mediated enhanced or reduced contaminant mobility. Such knowledge is of importance for a reliable assessment of contaminant fate and for the interpretation of laboratory and field scale data of contaminant transport and attenuation.

2.2.2.6 Role of nature of organic matter in soils and sediments

During the last 15 years huge differences in the sorption capacity of natural organic matter have be found for predominantly organic pollutants. Whereas on one hand differences in chemical composition and structure of the organic matter is discussed as being responsible for these differences more and more evidence appears showing the soils and sediments contain a complex mixture of particulate organic matter. Within this mixture carbonaceous particles predominate sorption of many hydrophobic organic compounds especially at low concentrations. Such carbonaceous particles comprise charcoal, bituminous coal fragments, all sorts of soot (all belonging to the ill defined group of black carbon). Methods to quantify the fraction of this highly reactive constituents in soils and sediments are lacking. Methods proposed so far are operationally defined which likely produces artefacts.

In addition, a fundamental understanding of the sorption mechanisms and kinetics in these carbonaceous phases is needed. This will help to explain the often observed but not understood sorption/desorption hysteresis in soils which is crucial to assess bioavailablity of sorbed pollutants. For that probe compounds have to be selected which allow to quantify sorption capacity and kinetics. Transfer functions have to be identified which allow to predict sorption behaviour of a whole class of pollutants based on measurements employing single or just a few probe compounds.

A complete lack exists concerning the long-term impact of weathering on these carbonaceous phases. This applies for carbon turnover rates (new data indicate that these type of carbon does not really participate in the carbon turnover in soils and sediment and is therefore termed dead carbon). Questions concerning the secondary release of pollutants associated with these carbonaceous phase upon weathering is completely open.

Most relevant scientific questions

2   Biogeochemical and physical processes (= WG3)

- How do soils '**process' pollutant inputs on the long-term**? What are the processes that lead to immobilisation ("aging") and/or mobilisation of pollutants (bioavailability / accessibility / transformation processes)? How does the interaction between dead and living organic matter work?

- What is the role of **"black carbon"** (organic matter formed during incomplete combustion of biomass) in the long-term in connection with release of strongly adsorbed organic pollutants?

- How can we a priori determine at a specific site whether **preferential flow** can occur? How important are mobile sorbents with regard to the fate and transport of pollutants? On which scales is this process relevant? How can the relevant vertical length be defined?

- Which are the **relevant processes at the ecosystem level** (e.g.: soil-vegetation-atmosphere interactions, hierarchical and dynamic root systems)? What is the role of **functional biodiversity** concerning fate of pollutants? Do feedback mechanisms exist?

- How do **climate and land-use changes affect soil functioning** (weathering, dissolution/precipitation of minerals, carbon turnover rates, release of DOC, wetting properties, permeability, …)?

Expert Statement

Winfried E.H. Blum, President of ECSSS, University of Natural Resources and Applied Life Sciences (BOKU), Vienna, Austria:
The protection of the soil and water system mainly depends on the capacity of soil to act as a sink for inorganic and organic pollutants, without losing its capacity to produce biomass or to sustain biodiversity. In this context, the spatial and the time scales of the different processes involved are of paramount importance. The main open questions regarding mineralisation and metabolisation processes of organics relate to the spatial soil conditions. For example it is known that these processes only occur in soil pores with a diameter greater than 0.5 µm, as microbes cannot enter smaller pores. In contrast, it is not well known how the transport of organics in larger pores determines the rate of microbiological processes.

Regarding inorganic pollutants, especially heavy metals, it is well known that these become less mobile in soils with time, which means that there must be immobilisation processes which are not yet identified in detail, such as diffusion of elements into the crystal structure of soil minerals, especially clay minerals and oxides, and the role of structural irregularities, e.g. replacement of certain elements during crystal formation. Without detailed knowledge about the capacity and velocity of such immobilisation processes, the environmental risk of pollution cannot be determined. Therefore these questions should be answered with priority.

3 Heterogeneity and scale issues in soil and groundwater

S. van der Zee, K. Jones, M. Jauzein

3.1 Overview

The scale problem permeates most theoretical and experimental research of the environmental compartments air, water, and soil (which each have biotic and abiotic sub-compartments). For this reason, a comprehensive overview of all processes and parameters involving scale issues is impossible. As a first step, the methodological approach is depicted and a number of important issues are discussed such as how to choose relevant scales explicitly accounting for governing processes and characteristic time scales.

The key issue of the scale problem, is that at different scales different processes are important. For this reason, different scale classifications have been proposed, where a well known classification has been given by Bouma and co-workers. In this classification, two major diagnostic properties or (axes) are distinguished, i.e., space and time. Obvious classes to be considered are:

Space: nm (molecular, double layer), µm (pore size), mm (soil organisms), meter (soil profile, pedon), field, region (watersheds, river basins), country, continent, mondial scale, where illustrations for a soil's perspective are given between brackets.
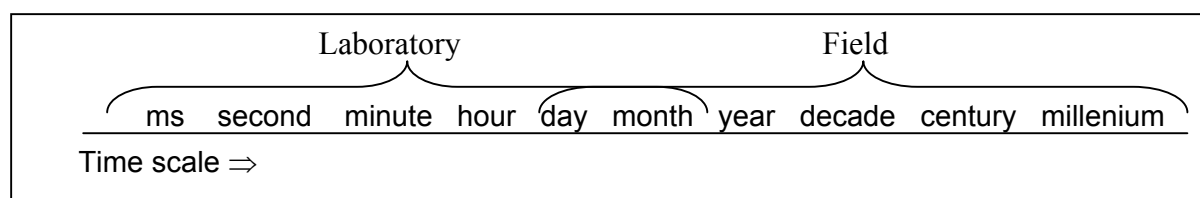
Figure 3.1: Resolution of time scales for laboratory and field studies

Though illustrative, such a classification remains somewhat arbitrary. For instance, one may be interested in studying river basin scales, which may be ranging from regional to continental sizes, yet are physically well distinguishable systems.

A more process oriented classification distinguishes the following scales:

1. scale of the natural medium and processes
2. scale of observation/experimentation
3. scale of modelling
4. scale of management and policy

This approach allows for anticipation of the difference of scales with respect to the system (1), activities (2 and 3), and demand (4). As modelling often is involved in 'interpretation' of experimental data, (2) and (3) may be combined. Here, this is not done, because of transparency reasons.

In the following paragraphs, scale issues are briefly discussed for different compartments.

3.2 State-of-the-art and research gaps / solution strategies

3.2.1 Physical properties and processes

Explicit attention for scaling issues has been predominantly given to the flow and transport of water and dissolved chemicals (solutes). Therefore, the experimental data base and the theoretical tools to jump between scales has advanced most for these issues.

A subject of study has been the moving between the scales of the individual pore to the continuum of a porous medium sample (a case of upscaling). Using different theoretical approaches (regularisation, averaging, normalisation, etc.) it has been shown, that the Kozeny-Carman equation that holds for the pore scale 'degenerates' to a expression that maintains only the first (order) term. Its applicability is limited (though still powerful for practice). Choosing different solutions for the closure problem, the higher order terms as well as the cross coupling effects can be addressed, at least in principle. The simplifications involved in this upscaling exercise, are again encountered when the Darcy equation needs to be upscaled from one continuum to a larger one with additional features: directional effects such as anisotropy may be the result of such additional features.

The hydraulic properties (saturated hydraulic conductivity [K_s] and permeability function [$k(\theta,p)$] and retention function [$p(\theta)$]) have been most commonly been assumed to conform to scale invariance (Miller similitude), by assuming a so-called scaling parameter [α] exists. This implies that media with different median grain sizes can be explicitly related with each other in terms of hydraulic properties if their scaling parameters are known. In that case, different media may have differently sized grains, but geometrically they are similar (one is a 'blown up' version of the other). For different soil samples (typically 100 cm^3) taken from a field or region, the scaling parameter has been found to be log-normally distributed in many cases. Generally, the geometrical similarity can not be maintained for such samples, but this scaling procedure provides a simple way to economically address variability at scales larger than 100 cm^3 (volumetrically), to give at least some attention to its effects.

As in most cases the scaling of hydraulic properties is pragmatic, rather than theoretically founded (on scale similarity), extrapolations to larger scales remain statistical extrapolations with inherent mechanistic uncertainties.

Besides laboratory approaches to assess hydraulic properties, also field scale measurements are possible. In principle, those are complicated by the same scale dependencies. For instance, the infiltro-meter/permeameter equipments may provide strongly different data if transposed over a short distance, e.g. if measurements are made in a fractured clay soil. Likewise, water-extraction based measurements such as with suction cups in the vadose zone, or with pumping wells in ground water, seldomly identify the origin of the extracted water. To be able to assess which proportion of the water is derived from more or less permeable sub-domains often remains obscure and would inevitably require additional information to make an educated guess. This implies, that the scale of the measurement tool is less than the scale of the typical medium variability (in one, two, or all three dimensions), and the implications for interpretation of the raw data as a base for management decisions, have hardly been brought into perspective yet.

Where the above scale issues have consequences for assessing water budgets for soils, ecosystems, and in agrometeorology, etc., they may have even larger consequences with regard to solute transport and the processes affected by solute transport.

The scale problem in solute transport allows for an illustration that has been well considered in the scientific literature. It is attractive to distinguish two scales, i.e., the scale of heterogeneity (X) and the scale of the considered system or domain (L). We may distinguish the following situations:

1) X and L are of similar size: then, the boundaries between different subdomains and the interaction between them must be deterministically known. Separate transport equations have to be formulated for each subdomain.

2) X < L: the heterogeneities may be described with simplified geometries (e.g. cubes, spheres) with average properties, and exchange between each 'aggregate' and macropores by diffusion has to be considered; sometimes a simple first order mass transfer may be appropriate.

3) X << L: the heterogeneities are visualised as a separate subdomain (or unspecified geometry) that exchanges with first order with the other subdomain (where fastest transport occurs).

4) X <<< L: the heterogeneity gives rise to additional dispersion but need not be considered as a subdomain (equilibrium assumption is valid for solute transport).

With the above distinguished four situations, it does not matter whether a flow in laboratory columns is considered, or flow and transport in an aquifer or a fracture rock system or even in a karst region. However, to assess which of the four cases holds, is not always simple. The main reason is that the scales as such are not the only factor of importance, since the rate of interaction/exchange between different sub-domains also affects when X is considered small, very small, et cetera.

3.2.2   Chemical properties and processes

The spatiotemporal variability of chemical properties and processes has received considerably less attention than e.g. hydrological and soil physical variability. Nevertheless, in the past two decades, attention has been given to the effect of spatial variability on chemical transport, taking both physical and chemical parameter variability into account. This has resulted in two main approaches of stochastic transport modeling, where either the temporal development of spatial moments or the temporal development of fluxes at a control plane were considered. One of the main conceptual approaches is called the stochastic convective SC model, in which local (small scale) dispersion is neglected, which leads to a parallel streamtube approximation.

In recent research (Van der Zee et al., 2004a,b; Acharya et al., 2004), a closer consideration was given to the transport of chemicals that are subject to nonlinear (biogeo)chemistry. This work has resulted in some remarkable conclusions. Thus, the upscaling step from the physically and/or chemically heterogeneous pore scale to the core (continuum; pore network) scale, has received attention for flow and for nonreactive transport. This established respectively that the flow equations differ for both scales (represented by the Cozeny-Karman (pore) and Darcy (core) equations), and that non-reactive transport at the core scale indeed obeys the Fickian behaviour of the Convection Dispersion Equation (CDE). For the case of nonlinear reactive transport, it became apparent that for a pore network the behaviour (at the core scale) does not obey the CDE. Moreover, it was shown with numerical calculations, that such transport also differs from the Travelling Wave TW behaviour, that should develop if the CDE is extended with a nonlinear reaction term (Van der Zee et al., 2004a, Acharya et al., 2004). The significant practical consequence of these conclusions is that both analytical solutions for nonlinear reactive transport are lacking and that the differential equation that governs core scale transport is not equal to the conventionally extended CDE. Hence, with the reservation that the pore networks were on the edge of ergodicity, it may be necessary that currently used commercial software (phreeq-models, MT3D-type of models) are in error.

In other work (Van der Zee et al., 2004b), the applicability of the SC model was assessed for the case of Monod kinetics affected biodegradation. For this case, initially resident microorganisms may degrade resident organic contaminant at the front of injected electron acceptor (e.g. oxygen or nitrate). In case of an autocorrelated random hydraulic conductivity field, a complex transport pattern develops, which depends sensitively on the magnitudes of the transversal dispersivity and transversal autocorrelation length. Depending on these magnitudes, either a travelling wave type of behaviour results at the large scale (dispersivity >> autocorrelation length), or Fickian behaviour (negligible dispersion), according to the SC model. Both regimes are separated by a transition regime. For the SC-regime, again may be concluded that the macroscopic scale is controlled by the CDE, and that nonlinearity of the (local, small scale) reactions is of no consequence whatsoever.

With these few illustrations, it has become clear that the large scale transport of reactive chemicals still has major unresolved conceptual issues, which need to be urgently addressed in view of the public demand to provide model answers at aquifer, or even watershed/river basin scales (in view of e.g. EU-calls in the 6/7th FP).

3.2.3   Biosphere scale-related properties and processes

Compared with soil physics and soil chemistry (including adjacent areas of hydrology, reservoir engineering, and geochemistry), the study of spatial variability in biology, ecology, ecotoxicology, is old. No doubt, that this is true because this research area has had an early focus on classification and

mapping, as is the case for traditional soil science and for geological mapping. Similar to those areas, however, the study of spatial variability was mainly implicit, as different ecotypes and ecotopes may have been recognised, and major processes may have been identified, but variability as such in relationship with that of the environment (soil, hydrology, etc.) was rarely considered.

For this reason, perhaps, there is much and advanced understanding of why certain vegetation is found on particular soils or under particular physico-chemical conditions, but causal quantitative relations with physico-chemical properties, processes and their variability have not been developed. In part, this may be due to soil physics and chemistry not being adjusted to help in unravelling such relationships. Nevertheless, this interaction between physical, chemical and biological processes and their variability should become a major and challenging focus for the next decades. As recent soil biological studies revealed, the concept of relevant scale may have to be developed first, because (geostatistical) tools may already be available, but the scaling-concepts are still lacking.

In view of contamination with biodegradable compounds, much work has been made of under-standing, assessing, and quantifying the biodegradation rate of such compounds as a function of their concentration, bioavailability, and to a lesser extent the environmental conditions such as trophic status. This has provided useful information, it does, however, not yet combine well with the physico-chemical aspects involved. These links require further attention.

Most relevant scientific questions

3   Heterogeneity and scale issues in soil and groundwater (=WG4)

- Which is a conceptual basis for **combining different sources of spatiotemporal variability** (physical, chemical, biological) for complex soil, groundwater and surface water systems?

- How to choose **relevant scales** explicitly accounting for governing processes incl. community ecology & ecosystem dynamics, and their characteristic **time scales**?

- Can we develop a **habitat-niche concept** for different organisms/plants in relation with spatio-temporal variability of physical and chemical conditions? How is this problem tackled in ecology at different scales and how can biotic/abiotic disciplines learn from each other?

- How can we identify processes from **data sets that combine interactions** between the soil food web/biology and physical/chemical properties in a designated soil volume and as a function of time (to serve as a data base on which to apply and test the development of first three identified research needs)?

- What are the **recent advances in remote sensing with regard to ecosystem variability** (physical, chemical, biological) that may provide breakthroughs in the near future (costs considered)?

4 Screening and monitoring tools at different scales

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4.1 Overview

Screening and monitoring tools are a prerequisite to measure and control physical and chemical soil degradation. However, the strategy needed to identify and quantity adverse effects and trends at different scales is for many situations still an open question.

To determine the diffuse input of a chemical into soil, e.g. the rate of atmospheric deposition, the amounts of fertiliser, sewage sludge, and organic wastes applied and the concentration of the chemical in these materials must be known. A major output flux from agricultural land is the export of the target chemical (or element) with harvesting. This output can be estimated if the amounts of crops harvested and the concentrations of the chemicals in them are known. Another output flux to be generally considered is leaching into the subsurface below the root zone.

Although the mass balance approach was frequently proposed as an important method to identify potential pollution, its practical application has been hampered by the lack of many of the required data at a national scale, be it because these data are not collected or be it that they are not made available due to legal restrictions or bureaucratic problems. Usually, the availability of monitoring data on input fluxes such as atmospheric deposition or use of agrochemicals is better on regional and national than on plot or field scale. In addition, data on output fluxes are scarce.

4.2 State-of-the-art and research gaps / solution strategies

4.2.1 Soil monitoring and screening

Currently, there is no Europe-wide monitoring network for soil, except for forest soils (ICP Forest, UNECE, see Tab. A3.3, Annex). Consequently, there is a lack of a consistent data set across Europe within as well as outside the EU. This results in a diversity of monitoring organisation schemes, range of parameters determined, frequency of sampling, and methods of analysis. In such systems, the transfer of data often is a problem. As a result of the diversity, there is a lack of harmonisation of the data derived from many national soil monitoring systems and there is no pan-European quality control of existing soil monitoring networks. Furthermore, in many countries two different systems for agricultural and forest soils exist. Some progress was achieved in monitoring of forest soils. Statutory soil monitoring is actually carried out in a number of EEA member countries (Tab. A3.3, Annex) but it is rarely suitable for the purposes of soil protection. The multi-functionality of soil requires more integrated approaches involving issues such as spatial planning, critical loads, and ecosystem analysis. The tools of spatial analysis as well as geo-referenced data such as high-resolution soil maps and digital evaluation models should be used. The utility of remote sensing data needs to be explored. Remote-sensing technology could be useful in assessing the actual state of land degradation or the amount of selected surface at a suitable territorial level – information which is still missing and which is difficult to obtain with traditional monitoring techniques.

The spatial variability of soils as well as the variability of soil contamination is very high. Therefore, a relatively dense measurement network is needed. If fast, simple, and cost-effective geophysical methods are used for the measurements of topsoil susceptibility and for a pre-screening, then a relative dense monitoring network can be applied in combination with a reduction of the number of samples and chemical analysis.

The following research needs can be identified:

- Harmonisation of measurement techniques and integration of various approaches adopted by individual countries to enable comparisons

- Harmonisation of the national monitoring networks and installation of a comprehensive Paneuropean Soil Monitoring Network based on existing European initiatives on soil monitoring (CORINE, LUCAS, ICPforests, INSPIRE etc.)

- Applying the predictive analysis for future risk assessment on a European level

- Studying prolonged effects of toxic substances on different soil ecosystems and the effect of the sudden or slow loose of the buffer capacity of soils due to the accumulation of heavy metals, organic compounds, and other pollutants ("ecological time bombe")

- Definition of a preliminary list of mandatory parameters and indicators chosen for diffuse contamination.

- Developing and applying techniques for monitoring radio-nuclides and soil solution chemistry

- Developing the fast and cost-effective on-site screening and monitoring techniques which will serve as an early warning system

- Undertake the intra-site geo-statistical data processing, especially for some easy detectable key soil parameters (e.g. particle size distribution, CEC, pH, EC, soil organic carbon, magnetic susceptibility) that could result in an improvement of the sampling design to detect actual changes within the soil as opposed to spatial variation (to make monitoring more sensitive to early changes)

Expert Statement

Robert Scholger, University of Leoben, Austria

Deposition of atmospheric particulates represents one of the most important contributions to environmental stresses and to human health hazards. Detailed and thorough knowledge of the pollution status and its development is of crucial importance to all institutions in concern; scientific and environmental as well as political. Without this knowledge it is impossible to develop and adopt the correct and efficient measures for sustainable industrial and social development.

Atmospheric particulates are mainly comprised of wind-blown soil and fly-ash particles emitted by industry and road traffic. Fly ashes contain a significant portion of toxic heavy metals in particle sizes that can be respired. Besides that, fly ashes contain also ferrimagnetic particles, particularly magnetite and hematite. These magnetic particles are produced during combustion of fossil fuel, metallurgical processes, cement production, etc., and emitted, transported through the atmosphere and deposited along with heavy metals.

Several studies have shown that a close relation exists between the distribution of magnetic particles and the distribution of heavy metals around industrial sites. Though it is widely accepted now that magnetic parameters can be used as a proxy for heavy metal concentrations, the physico-chemical relations are not fully understood. The type of relation between the heavy metals and the magnetic material might depend on the process during which they were produced. Solid solution, surface adsorption or mere coexistence are possible.

No study published so far deals with the relation between heavy metals and magnetic material in dependence on the production process. Knowledge of these relations and of the exact magnetic status of the ferrimagnetics is crucial for the quantification of the ferrimagnetics and for their use to detect critical values of concentrations of heavy metals. The effectiveness of the magnetic method can then be explained physically/chemically and the monitoring potential of soil magnetic measurements will increase from a proxy to a more quantitative method.

4.2.2   Material fluxes in soil pollution monitoring

For more than a decade, scientists have proposed to use balances of material fluxes in soil pollution monitoring and carried out work to provide a scientific basis for this approach (see Schulin 1993). Even though the basic idea is simple, the application of mass flux balancing as a routine tool in soil monitoring networks is facing considerable practical problems. Firstly, the spatial and temporal resolutions at which fluxes can and should be assessed are still crucial questions (Baccini and von Steiger 1993, Keller et al. 2001, Schulin 2003). Fluxes of contaminants relate to different spatial scales (field, farm, region) and periods (day, crop rotation, year). The local assessment of a complete material flux balance requires information the collection of which can be afforded in the framework of a particular scientific investigation, but not on a routine basis of a monitoring network. For the latter purpose, regional or larger scales are in general easier to handle.

Apart from the scale issue, also many other points remain to be clarified. A point closely related to the problem of scale disparity is the problem of spatial and temporal variability. This may be a problem even for the assessment of atmospheric deposition fluxes which are often considered as rather homogeneous locally. However, there is little information about the small-scale variation of airborne deposition, and this information rather suggests that the local variability of this flux can be considerable. Output via erosion is commonly not considered, but may play an important role on small plots. Output through harvesting is the best known process. Output fluxes across the lower boundary of the soil compartment are particularly difficult to determine. One problem involved here is that this boundary depends on the distribution of roots and may vary with the types of plants being cultivated and with the agricultural treatment.

A basic problem of the mass flux balance approach is that many fluxes cannot be determined directly, but have to be inferred from data on the fluxes of products containing the target component and the concentration of this component in the product. For example output fluxes of metals associated with the harvest of crops are calculated by multiplying the cumulated flux of the crop exported from the field with the metal concentration of the crop. The problem arises from the fact that these concentrations can vary considerably and that in general using estimates of average concentrations is the best what is possible. If concentrations do not vary independently of fluxes, this can result in considerable error, which increases with increasing correlation and increasing fluctuation (Keller, 2000). Given the many problems to obtain detailed, complete and reliable data and thus the need to fill the gaps with estimates, which requires to make many implicit or explicit assumptions, it is rather surprising that error, uncertainty and sensitivity analysis are aspects which are by far not adequately addressed or even completely neglected in most studies on mass flux monitoring. Recent work has shown how a scientifically sound assessment of the uncertainty of element balances in agro-ecosystems can be achieved on regional scales using standard stochastic methods such as Monte Carlo simulation and error propagation calculus to account for input data and model parameter uncertainty (Keller et al., 2002, Keller and Schulin, 2003).

The following research needs can be identified:

- Mass flux monitoring: Identification of small-scale variation of airborne deposition and of error, uncertainty and sensitivity analysis

- Quantification of output fluxes across the lower boundary of the soil compartment in dependance on the distribution of roots and plants

- Scientifically sound assessment of the uncertainty and sensitivity of element balances in agro-ecosystems on different scales

See also 4.3, where results of an inquiry on monitoring activities in Europe (mass balances and emerging pollutants) are reported.

4.2.3   Sampling and sample preparation procedures

Sampling and sample preparation is the most laborious process in chemical analysis and typically accounts for more than 75% of analysis time. The analysis of trace components in complex environmental matrices requires multi-step sample preparation. The general problem in analysis of complex environmental samples is that the extract obtained by exhaustive extraction techniques typically contains a large number of matrix components, which may co-elute with the analytes and disturb the quantitative analysis. The presence of interfering substances demands either a very selective detection, or tedious extract clean up, or even both. Generally, multi-step sample pre-treatment which aims at the reduction of the matrix content and the enrichment of the target compounds still remains as the most direct means of obtaining maximum sensitivity. However, extraction and clean-up protocols used are time and labour consuming, and they often constitute the bottleneck of the analytical method. Tab. A3.4.1 in the Annex provides an overview over standardised sampling guidances, Tab. A3.4.2 over analytical methods on inorganic compounds.

The growing number of samples to be analysed in laboratories carrying out monitoring studies requires the employment of high-throughput and fully automated analytical techniques. Because of these reasons, it is necessary to concentrate the effort into the development of cost-effective sample handling techniques characterised by the efficiency and simplicity of operations and devices. The most important research needs in environmental analytical chemistry in the future are:

- Application of highly specific tailored sorbents (i.e. molecular imprinted polymers, immuno-sorbents, restricted access materials) for solid phase extraction

- Integration of several sample preparation steps into one step (i.e. application of passive samplers for simultaneous sampling, extraction and enrichment of pollutants from liquid and gaseous samples and Matrix Solid-Phase Dispersion (MSPD) for biological matrices)

- Automation through coupling of sample preparation units and detection systems (i.e. on-line solid phase extraction (SPE)-LC, on-line solid phase micro extraction (SPME)-GC and SPME-LC)

- More common application of passive sampling such as SPMD, ceramic dosimeters, extractions cartridges for atmospheric deposition and water

4.2.4   Detection of organic pollutants

Methods for determination of hydrophobic organic compounds in water and wastewater usually comprise stages of separating the contaminants from water or wastewater and next quantitative analysis. The gas chromatography technique is usually used as the method of quantitative analysis using a mass spectrometer (GC/MS) or an electron capture detector (GC/ECD). In case of halogenated derivatives of aliphatic hydrocarbons, the methods are usually based on the technique of direct dosage of a sample, solid phase micro-extraction (SPME) or purge and trap thermal desorption. Chlorophenols are usually determined by means of the gas chromatography (GC) and liquid chromatography (HPLC). In the GC, the most often used detectors are an electron capture detector (GC/ECD) or a mass spectrometer (GC/MS). Detection in HPLC is performed by the UV/VIS, fluorescence, electrochemical (ED) or atmospheric pressure chemical ionisation mass spectrometer (LC-API-MS) detectors.

In general, all the ISO methods and procedures are very expensive (instrumentation, materials, high-qualified service). There are needs to develop analytical methods that are faster, simpler and more sensitive including also techniques that could be applied directly in the field for fast and cost effective pre-screening or monitoring and early warning systems. Impressive improvements in detection limits for organic contaminants have pushed the target concentrations in aqueous samples from the microgram to the nanogram, or picogram per liter range. Detection of sub-ppt concentrations is becoming routine for many organic analytes and methods achieving detection of a few hundred femtograms of some analytes have been reported. Such progress is mostly due to development of hyphenated chromatography-mass spectrometry (MS) techniques, which are today the methods of choice for the determination of trace organic analytes in environmental samples.

Currently the main breakthrough is observed in the application of LC-MS and LC-MS-MS techniques. One of the obstacles to routine analytical applications of LC-MS had been the unavailability of rugged and reliable LC-MS interfaces. The development of atmospheric pressure ionisation (API) overcame such limitations as poor structural information, or sensitivity seen with thermo-spray (TSP), or particle-beam (PB), respectively. API is used as a generic term for soft ionisation obtained by different interface/ionisation types, such as atmospheric pressure chemical ionisation (APCI) and electro-spray (ESI) that operate under atmospheric pressure conditions. Today, LC-MS has become a routine analytical tool, allowing the detection of polar and non-volatile compounds not amenable to GC analysis.

A few in-situ chemical monitoring systems exist, but they do not attempt to quantify or characterise the contaminant (e.g., location, composition, etc.). There is a need to develop a micro-sensor monitoring system that can be used to monitor organic pollution (e.g. VOCs) in the subsurface. Ability of in situ application method using the micro-chemical sensors has to be tested.

The next challenge is to develop uniform techniques for detection of emerging contaminants including surfactants and surfactant residues (Petrovic and Barcelo 2004), pharmaceuticals and personal care products, gasoline additives, flame retardants, plasticisers, etc. These contaminants are mainly composed of products used in everyday life and are mostly unregulated by national and international law but have to be considered for future regulation depending on their potential health effects and monitoring data regarding their occurrence in the environment.

Summarising, the most important research needs in this area can be focused on:

- More common use of biosensors for water and soil organic pollution control

- Development of a micro-sensor monitoring system that can be used to monitor organic pollution (e.g. VOCs)

- Development of in-situ chemical monitoring systems as Catalytic Bead Sensors, Metal-Oxide Semiconductor Sensors and Infrared Sensors for quantify or characterise the contaminant (e.g., location, composition, etc.)

- Development of uniform techniques for detection of emerging contaminants

- Provision of new soil assessment systems (e.g., technologies based on resin capsule "adsorbers")

- Application in soil pollution study high-throughput chemical analysis using μChemLab

4.2.5 Detection of inorganic pollutants

Actually most of ISO regulation is in preparation or revising state (see Annex, Tab. A3.4.3). Only the detection of some heavy metals is regulated already by ISO (Cd, Cr, Co, Cu, Pb, Mn, Ni and Zn). For the others various national standards are in use. Actually prepared ISO standards will cover the uniform procedure for determination of total element content. Also determination of such dangerous compounds as Hg, Tl, As and cyanide content will be standardised.

The open question is still the extraction procedure. The determination of total content of heavy metal following the aqua regia procedure is not sufficient for the prediction of the fate and behaviour of the compound of interest in the environment. For these purposes, the extraction in nitrous acid that gives more information about the availability of elements for plants is more useful. Additionally, sequential or selective extraction analysis give more information about forms of heavy metals and chemical bounding and is preferred by soil scientists.

Also the same problem as in case of organic pollutants is the lack of cost effective fast screening method very useful for monitoring and early warning.

Innovative methods are:

- Magnetometry (used as a tracer of heavy metal site contamination)

- Bacterial sensors / bioluminescence (Cd, Zn, Cr, Hg)

- WECSA Soil Access System (PST1 resin capsule for K, S, P NO₃, NH₄, Ca, Mg, Na, Mn, Fe, Zn, Cu, Pb, Hg detection)

- Heavy metal analyser HEMA 2002

- Catalytic Adsorptive Striping Voltametry

The Water Frame Directive and the Soil Thematic Strategy determine the most urgent needs for assessing and monitoring quality and quality changes of the water-soil-sediment-air system. As many as possible environmental compounds have to be tested and monitored. The list of pollutants is still increasing. Taking into consideration both, economical costs of quality and sensitivity development with increasing demand for their quantity, then it is necessary to apply relatively inexpensive field techniques for environmental site assessment and pollution detection. The innovative techniques could be considered in 4 groups according to their place in stepwise procedure for screening, monitoring, and testing:

- Remote sensing for large scale overview and monitoring changes

- Proxy methods for regional scale overview and selection of sampling points

- On site sensors for fast estimation of pollution (quality and quantity)

- Sampling and analysis for individual pollutants

Most relevant scientific questions

4   Screening and monitoring tools at different scales (=WG 2)

- How can we **identify and quantify adverse effects and trends** (e.g. by time or spatial integration or measurements of proxies; mechanisms of perception (who, how, when...))?

- What are **suitable proxies** to quantify pollution and indicators for soil quality and functioning? Which **environmental tracers** could be used for a better understanding of the soil system?

- How can the appropriate design for **data acquisition at different scales be controlled**?

- Which **analytical techniques** are needed for **cost-effective screening and monitoring** of known and emerging compounds? How can these techniques be validated (field and lab)?

4.3   Mass balances and emerging contaminants in soils - results of inquiries on monitoring activities in Europe

4.3.1   Introduction / Inquiry by the EEA

The proposal for monitoring European soils (EEA, 2001a) was discussed at the first EIONET (European Environmental Information and Observation Network) workshop on soil (EEA, 2001b). This has led to the formation of three working groups on indicators of those threats that were considered most important, i. e. soil sealing, soil erosion, and soil contamination - both local and diffuse. The conclusions of the working group on soil contamination were discussed at an EIONET

workshop held in Vienna 2001 (EEA, 2001a,b). Diffuse contamination originating from air pollution, agricultural application of fertilisers and sewage sludge, and uncontrolled waste disposal was recognised as a major environmental problem.

Half of the countries responding to an EEA-inquiry (EEA 2001b) considered short-term diffuse contamination and most of them also long-term diffuse contamination as a high priority problem. On the other hand, only one third of the countries could deliver relevant data.

The inquiry also revealed that soil pollution is generally assessed by comparing pollutant concentrations in soils with standard values such as target, threshold and background values. The substances under survey are primarily heavy metals, PAHs, and pesticides. Emerging contaminants are only mentioned in one table of the report, but not within the text, even though identifying new chemicals that may contaminate soil and should therefore be monitored, is crucial for prevention of future problems arising from such contamination.

It was recommended that in addition to concentrations, also fluxes of contaminants into soil should be assessed, because diffuse pollutant concentrations in soils in general change very slowly. Variations between repeated analyses are often larger than the changes in soils over 5 or 10 years. Determination of fluxes would allow to detect and to react to soil pollution already at an early state. Furthermore, information on fluxes can give early hints when ground or surface waters are most likely at risk to be contaminated in the future.

In Germany for example, 794 agricultural, forest and municipal monitoring sites have been established at which concentrations as well as inputs and outputs of contaminants are recorded.

To report on the state of the environment, the EEA has chosen an indicator-based approach. During the EIONET workshop on indicators for soil contamination, a preliminary list of indicators on soil contamination for localised and diffuse sources was discussed (EEA 2002).

Seven indicators were judged to be of high and upper-medium importance, including i) exceedance of critical limits of heavy metal contents and ii) heavy metal balances. However, no data were available for either of these indicators at a European level.

More than half of the countries participating in the EEA-inquiry have established critical limits for heavy metal concentrations in soil. The list of target heavy metals generally includes Pb, Cd, Hg and often also Cu, Ni, and Zn.

A report on monitoring activities in 32 countries has recently been compiled by Peijnenburg et al. (2004) on behalf of the EEA.

4.3.2   Inquiry by SOWA

In order to get information about strategies in place or planned to reduce the fluxes of potentially harmful substances and to monitor emerging pollutants in different European countries, an inquiry was conducted by B. Buchter and L. Matile from SOWA-Partner 3, ETH Zurich during November 2004. The following questions were asked to Soil Protection Authorities of 17 countries:

We are collecting information on strategies and ideas in connection with diffusive, extensive soil pollution. Mainly, we would like to know whether there exist alternative solutions to the critical load approach to regulate or even reduce the fluxes of potentially harmful substances with the aim of limiting their accumulation in the soil.

1) Do approaches exist in your country to control fluxes of potentially harmful substances other than with guide/intervention values?

Furthermore, we are looking for soil monitoring projects for pollutants that are either not (yet) or only recently regulated by law, sometimes called emerging contaminants (e.g., pesticides, hormones, antibiotics, x-ray contrasts, sun creme additives, flame retardants).

2) Do you know of soil monitoring projects, either national or regional or concerning special objects (lakes, rivers), being planned in your country for the chemicals mentioned above?

4.3.3   Answers

The specific reports on the monitoring of diffuse pollution and relevant internet addresses of the participating authorities of different European countries are compiled in Annex A1.3 and A2.

4.3.3.1 Austria

To question 1:

Under the acronym MONORPOP, an INTERREG IIIB project has been initiated. No results are so far available. Information will soon be given (www.monarpop.at). Airborne input of heavy metals (Pb, Cd, Ni, Cr, Co, Zn) has been monitored by analysing moss at more than 200 sites.

To question 2:

Comprehensive information is given in the Seventh State of the Environment Report (7. Umwelt-kontrollbericht). Soil protection in Austria is organised by the States ("Länder"). There are no federal regulations with regard to soil protection. Therefore, the pollutants being measured differ within Austria. Five States have passed soil protection acts. Austria-wide information is available from the database BORIS where data on soil condition have been merged and put in a uniform form. All over Austria, heavy metals in soils are monitored at more than 2000 sites. Some of the provinces also analysed organic pollutants such as pesticides, PCBs, and PAHs. These measurements have not been repeated so far. The number of sites is about 600.

Furthermore, some States have established permanent monitoring sites where some organic pollutants like PAHs, PCBs, and dioxins are analysed for the first time. Which pollutants will be analysed is, however, not yet fixed. There is no agreement on a list of persistent organic pollutants as a minimum requirement for soil inventories and/or soil monitoring sites.

4.3.3.2 Germany

To question 1:

The idea of controlling the mass balance of pollutants to limit their content in agricultural soils has resulted in four different action options discussed in a strategy report: 1) no pollutants at all (for special chemicals only), 2) pollutant content of the material added (fertiliser, sewage sludge) equals that of the soil, 3) input not greater than output, 4) threshold values as guidelines. The flux of heavy metals is limited by option 2, which is somehow equivalent to option 3, but easier to handle. The estimated fluxes based on option 2 revealed that the tolerable contents of heavy metals in fertilisers should be reduced. Other contaminants such as PAH, PCB, and PCDD/F are also discussed in the report, but not included in the calculation for maximum tolerable contents. The Federal Soil Protection and Contaminated Sites Ordinance already restricts the maximum flux of 7 heavy metals. However, these values are larger than those in the strategy report.

To question 2:

Across Germany, heavy metal content of soils is monitored at about 800 sites. Some of the States also analysed organic pollutants such as pesticides, PCBs, and PAHs. Different organic pollutants including musk compounds in sewage sludge and their behaviour in the soil are analysed in single projects but not monitored.

4.3.3.3 The Netherlands

To question 1: -

To question 2:

There is no monitoring network for emerging contaminants in soils. However, the total toxicity of big rivers is being monitored, without identification of the toxicants (participating authorities: RIZA and

RIVM). Furthermore, there are monitoring networks for soil and water quality, and RIVM together with Alterra runs a national ecological soil-monitoring project.

A RIVM-report has recently been finished, which will be published as a EEA-report, on monitoring of chemicals in the environment. Information about monitoring activities in 32 countries has been collected and stored electronically (see A1.3, "Netherlands"). The report reveals that only the air and partially the water compartments are monitored across Europe in a similar quality and quantity, whereas the information on all other compartments, soil included, is patchy and not at all complete. In many countries, pesticides, which have been banned, are included but new substitutes, often equally or even more toxic, are not (yet) included.

4.3.3.4 Sweden

To question 1:

Fluxes of potentially harmful substances are controlled with guide/intervention values. There exist no other approaches.

Brominated flame retardants (i.e. PBDE, HBCD) are regularly monitored in fish, sediment, blue mussel, guillemot eggs, and mother milk.

Agricultural pesticides are regularly monitored in surface water, deposition and ground water.

Some antibiotics are regularly measured in sludge from sewage treatment plants (7 locations).

To question 2:

As part of a screening programme in 2005, substances such as biocides, hormones, and pharmaceuticals will be determined in the water environment, but not in the soil.

In earlier years substances have been chosen for screening, including phenolic substances, other types of flame retardants, chlorinated paraffines, fluorinated compounds. Usually no soil samples have been taken.

4.3.3.5 Switzerland

To question 1:

The legal regulations for fertiliser and pesticide applications on agricultural land are currently in revision in Switzerland. The revision will affect a number of guide values and recommendations for environmental sound agricultural practice.

A potentially very effective instrument to influence inputs of chemicals into agricultural soils are subsidies paid by the state for measures considered to have an ecological benefit and to improve the quality of the environment. These payments are made on the condition of a balanced P and N farm budget (±10 %). This restriction also influences the input of other compounds by animal manure and mineral fertilizer.

Heavy metal balances of 48 agricultural sites of the Swiss Soil Monitoring Network (NABO) are being assessed since 1996. The NABO comprises 105 sites across Switzerland with various land use characteristics. Spatial and temporal variation of model input parameters and data uncertainty are taken into account. The approach considers inputs by animal manure, mineral and waste fertilizers, pesticides and atmospheric deposition as well as outputs by crops. For each site the data for the amounts of the fertilizers and harvest are gathered annually.

To question 2:

PAH, dioxins and PCB concentrations in soil are regulated by the Swiss Federal Ordinance relating to Impacts on Soil, issued in 1998. These compounds have been measured at numerous sites of the national and cantonal soil monitoring networks. Currently the quality assurance for these compounds

regarding the sampling procedure and chemical analysis is being evaluated. In the future, measurement of these compounds will be included in the monitoring program.

However, there is no national strategy to identify emerging contaminants in soils. Due to the lack of a comprehensive environmental monitoring concept, there is also little coordination between soil monitoring and other environmental monitoring activities.

4.3.3.6 United Kingdom

To question 1: -

To question 2:

DEFRA and the Environment Agency will soon be starting a project to assess sources of current and potential contamination of soils and their impacts on soil functions. Target chemicals include heavy metals, radionuclides, and persistent organic and inorganic compounds.

A project is currently being undertaken on heavy metal contamination of soils and their impacts on microbial soil functions, in particular with respect to sewage sludge application on agricultural land.

The Environment Agency is also undertaking a project on measuring the content of dioxins and furans, PCBs, PAHs and heavy metals in soil and herbage. However, this is a base-line survey and therefore may not be repeated in the foreseeable future.

The Environment Agency has completed some work on emerging contaminants in water.

Table 4.1: Sources of information of countries who responded to the inquiry

Country	Institution	Person	Address
Austria	Umweltbundesamt Wien	Mr Huber Mrs Freudenschuss	boden@umweltbundesamt.at huber@ubavie.gv.at alexandra.freudenschuss@umweltbundesamt.at
Germany	Umweltbundesamt Berlin	Mr Glante Mrs Werner Mrs Vogel	frank.glante@uba.de beate.werner@uba.de ines.vogel@uba.de
Netherlands	RIVM research for man and environment	Mrs Soczo Mr Breure Mr Peijnenburg	info@rivm.nl esther.soczo@rivm.nl Ton.Breure@rivm.nl WJGM.Peijnenburg@rivm.nl
Sweden	Swedish Environmental Protection Agency	Ms Nerkegard Mrs Hedlund Mr Marklund	Lena.nerkegard@naturvardsverket.se britta.hedlund@environ.se hakan.marklund@naturvardsverket.se
Switzerland	Agroscope FAL Reckenholz	Armin Keller	armin.keller@fal.admin.ch
UK	Department for Environment Food and Rural Affairs	Mrs Taylor Mrs Morris Mr Brighty	soils@defra.gsi.gov.uk rebecca.c.taylor@DEFRA.GSI.GOV.UK jane.morris@environment-agency.gov.uk geoff.brighty@environment-agency.gov.uk

5 Management options for large scale soil and water pollution incl. environmental economics / socio-economic issues

R. Schulin, T. Stoll, E. Hepperle, S. Gupta, P. Grathwohl, D. Halm, K.-U. Totsche, W. Walther, C. Konrad

5.1 Overview

Large areas of agricultural land are affected by pollution associated with certain cultivation practices (use of pesticides, application of commercial fertilisers, manure, sewage sludge etc.) as well as by atmospheric deposition. These areas pose a great challenge with respect to the assessment of ecological and human health risks, management, and treatment.

Continuing low-rate pollution of soils, sediments and aquifers presents a particular type of environmental problem. Slow accumulation is difficult to detect over short time spans. Gradually, the pollution will spread into other compartments and enter the food chains. Unlike hot spots, i.e. high levels of contamination concentrated in small areas, such contamination has little potential to result in acute problems. But due to the large areas affected by this type of pollution, the effects are as ubiquitous as its dispersion and have much less possibility of dilution or compensation from adjacent unaffected areas than hot spot pollution. If occurring at a large scale, already moderate accumulation of xenobiotics, metals or nutrients such as N, P, Ca, Mg, and S can seriously disturb ecological processes and impair life-supporting ecosystem functions, threaten the quality of food and fodder products and result in long-lasting pollution of ground and surface waters.

According to the results of the Swiss Monitoring and Surveillance Program (NABO) approximately 10% of the agricultural soils exceed one or several guide values for heavy metals in topsoils. According to the Swiss legislation on the environment, the exceedance of a guide value means that the ecological quality of the respective soil is not warranted in the long run.

In Germany the average deposition of heavy metals ranged between 100 and 200 mg m^{-2} a^{-1} from 1994 to 1998. Much less solid data are available on the release of organic pollutants into the environment. In 1998 approximately 320,000 t of pesticides were marketed in the European Union.

Frequently applied pesticides are regularly found in groundwater although their licensing for the market requires extensive laboratory testing. The waters pumped by extraction wells of many large waterworks is contaminated by pesticides. Between 20 and 30 of the most important agents have been found in around 10 % of the monitoring wells of several regions in Western Europe. The behaviour and fate of these pesticides in soils and groundwater is still far from being sufficiently understood.

Organic pollutants are by far not the whole story with respect to diffuse groundwater pollution. In many rural regions of Western Europe, the production of drinking water from groundwater has to cope with nitrate pollution. Processes such as denitrification have to be employed to eliminate excessive nitrate. Denitrification depends on the availability of metabolic energy sources such as organic carbon or sulfides, e.g. such as pyrite. The stocks of these materials limit the life time of the process and, thus, also the life times of the water works at such sites. Increasing concentrations of nitrate in groundwater are often followed by increases in sulfate, water hardness and trace elements, e.g. cadmium, arsenic, and nickel.

Apart from nitrogen also phosphorus is a macro-nutrient which poses serious pollution problems not only to surface, but also groundwaters. In some regions with intensive animal husbandry P inputs into soils have accumulated to an extent that the sorption capacity of the soil for P is saturated so that further inputs are no longer retained by the soil, but leached towards the groundwater.

Sustainable land use requires active or passive control of large-scale diffuse matter fluxes into, within and out of agro-ecosystems. This calls for effective methods and tools to monitor these fluxes, to assess the effects caused by low-rate large-scale accumulation of pollutants, and to develop strategies and techniques to prevent and decrease this type of pollution. In addition there is the challenging task to treat already affected soils and waters. Successful large-scale and long-term management of

material fluxes in agro-ecosystems and of land affected by diffuse low to medium-level pollution cannot be achieved by the same strategies and methods developed for the detection, classification and treatment of hot spot contamination such as hazardous waste sites. It requires the development of suitable tools to:

- survey and monitor the state and development of soil and water pollution
- understand the environmental behaviour and fate of the pollutants
- assess and evaluate the ecological, economical and toxicological risks
- develop problem-adequate abatement, management and remediation strategies.

5.2 State-of-the-art and research gaps / solution strategies

5.2.1 Survey and monitoring of the state and development of soil and water pollution

Any policy, management strategy or other measure to control diffuse soil and water pollution can only be successful in the long run, if the state of the pollution is monitored and trends of future development are detected at an early stage. This information is necessary to 1) target measures effectively and 2) control the success of the interventions.

5.2.1.1 Monitoring the state and spatial distribution of diffuse pollution

Many European states, e.g. Germany, Austria, The Netherlands and Switzerland, have established soil and groundwater monitoring programmes. These programmes vary considerably with respect to their strategy, the monitored parameters, the employed sampling and analytical methods, the design and density of the sampling grid and the intervals between surveys. In general, only a few trace metals and macro-nutrients are monitored, and usually only total concentrations and no bioavailable or mobile fractions are determined.

Example: Monitoring of diffuse soil and groundwater pollution in Switzerland:

The Swiss National Soil Surveillance and Monitoring Programme (NABO) was established in 1986. In the meantime topsoil metal concentrations have been determined in three repetitive surveys. At present the network includes 105 selected locations representing sites exposed to diffuse pollution sources. There are no clear trends recognisable yet due to high local variations from sampling to sampling. For the future it is planned also to include persistent organic pollutants (POP) into the programme.

The National Programme for the Monitoring of Groundwater Quality (NAQUA) was established in 1997. Around 50 points are sampled regularly. For the investigation of specific problems the number of measurement points can be expanded to 500.
In 2002, pesticide residues have been found at more than 50% of 390 investigated points. At 20 points (i.e. at around 10% of all points), the concentrations exceeded legal limit values.

These programmes give a good overview of the overall situation with respect to the pollutants under survey, but the spatial sampling densities of the networks are not sufficient to allow mapping. Maps are, however, needed in order to adequately account for the distribution of contamination in the management of the land. The required spatial resolution depends on the intended use of that information. In mapping soil and groundwater pollution the problem is to extrapolate or predict the pollution in the areas between the points at which it has actually been measured. The accuracy of the prediction depends on the design of the sampling grid, in particular the density of the sampled points, the spatial structure of the variability and the availability of additional information with indicator value for the state of pollution. Land use data are particularly valuable for this purpose in groundwater as

well as soil pollution surveying. In addition, the following proxy methods have been proposed to improve soil pollution mapping: geomagnetics, biosensors, remote sensing and historical information on land use (e.g. application of copper sulfate in vineyards, reclamation of former industrial areas, waste disposal sites). Geostatistics provides methods to make optimum use of available data in the analysis and mapping of the spatial distributions.

5.2.1.2 Mass flux balances: a tool to detect and to control the accumulation of pollution

The knowledge of the material fluxes is very important in assessing the development of a pollution situation and its potential impacts. Mass balances schemes and material flux models determine, analyse and predict pollutant accumulation in soil. Material fluxes in agricultural soils vary considerably in space and time depending on factors such as types of farms, types of cultivation practices, number of animals per unit area, production of animal manure per unit area of farm. Keller (2000) found that net accumulation of cadmium in agricultural soils varied between 0.6 and 17.8 g ha^1 a^{-1} and zinc accumulation between 17.9 and 3360 g ha^{-1} a^{-1} in a rural region of Switzerland.

Another question to be solved is the deposition (by erosion and/or runoff) and the re-use of excavated soil like materials/sediments. In addition, the influence of background geogenic loads and the impact of current and historical land uses on soil quality are not being systematically investigated and interpreted except at dumping sites.

5.2.2   Environmental behaviour and fate of the pollutants

Attempts to control the nitrate problem in most cases did not regard chemical and biological processes in aquifers such as interactions between solution phase and rock matrix and denitrification.

The elimination of undesired macro-nutrients in aquifers such as nitrate depends on the availability of biochemical reaction partners such as organic carbon or iron sulfides, their spatial distribution in relation to flows, and the rates of fluxes. Mostly, the properties of the aquifer due to attenuation are unknown and the processes running in the aquifer can mathematically only be expressed inadequately.

Figure 5.2 schematically shows a nitrate plume approaching an extraction well. Figure 5.3 shows how the plume can be stopped by a permeable layer that contains electron donors (reactive material). Nitrate is eliminated in this layer by denitrification, which occurs because of the presence of the reactive material.

The aquifer is handled as a black box. The knowledge about the mechanisms of reaction that lead to a decrease of unwanted concentrations, their spatial subterranean distribution and life span that lead to a decrease of unwanted concentrations are vital for the planning and operation of water extraction plants. If it is diagnosed that the elimination capacity of the aquifer is limited, these findings have influence on decisions on which treatment techniques will have to be employed in the waterworks and on which plots of land measures have to be taken in order to secure future water supply.

The preparation of maps of "vulnerability of aquifers" (e.g. in Germany developed by the geological surveys) can show the potential of natural attenuation to eliminate specific substances. Up to now, this geopotential, e.g. for nitrate elimination is rarely considered during the planning of the land use up to now.

The processes of natural attenuation of macro-nutrients in aquifers, their spatial distribution and their lifespan are still unknown to a large extent. There is a great need for research in this field to expand the knowledge required to protect groundwater and the capacity of aquifers to eliminate or attenuate pollutants. Such knowledge is an essential basis for a sustainable management of drinking water resources.
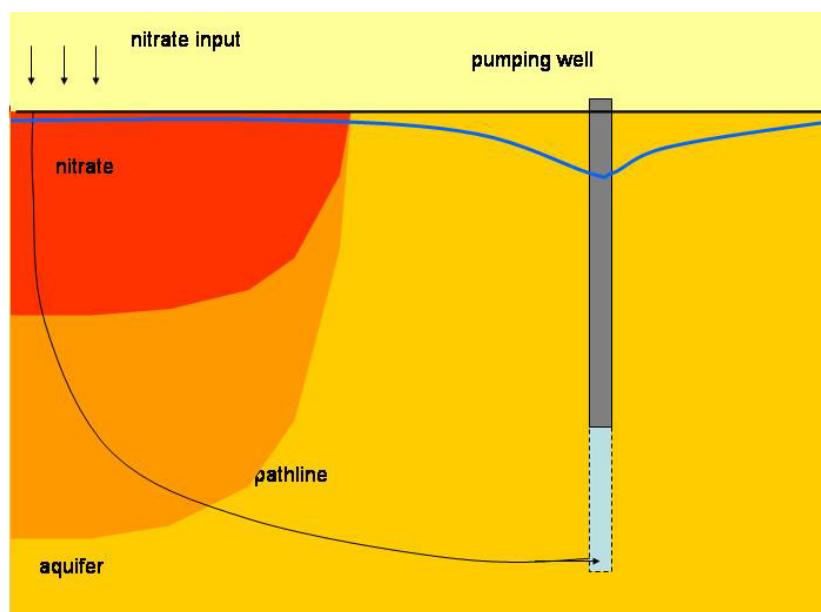
Figure 5.2: nitrate input in an aquifer and transport without nitrate elimination by reactive materials
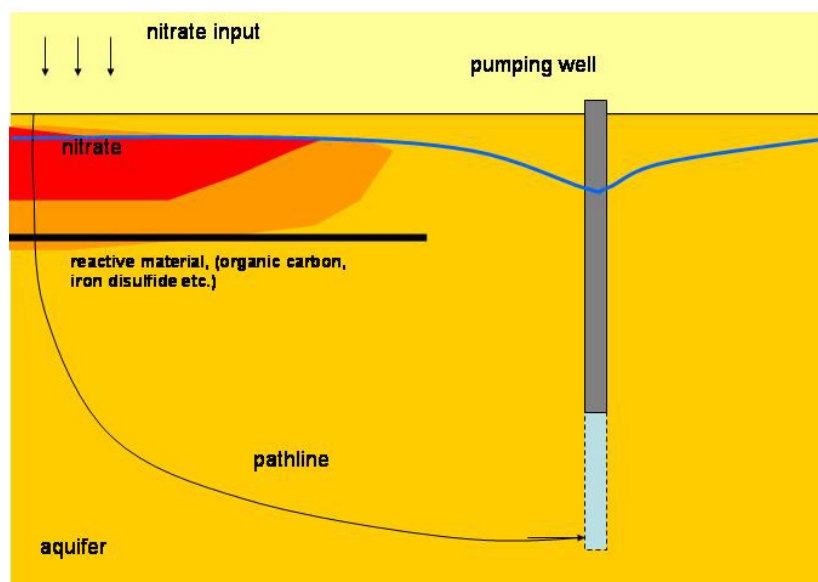
Figure 5.3: Nitrate input in an aquifer and transport with nitrate elimination by reactive materials

5.2.3   Assessment and evaluation of effects of diffuse soil and water pollution

The evaluation of soil and water pollution can be based on:

- Transfer into the food chain and toxicity risks for humans, animals and plants

- Transfer and potential effects in other compartments

- Degradation of soil quality, e.g. for plant production

- Degradation of groundwater quality and elimination capacity of the aquifer

- Disturbance of ecosystem properties, e.g. population community structures, and ecosystem functions such as organic matter decomposition

Diffuse pollution by macro-nutrients can not only disturb ecological processes but also damage the physical properties of the subsurface. Aquifers are oligotrophic ecological systems. There is considerable concern that similar effects of the eutrophication will occur as in the past in oligotrophic surface waters such as lakes. Increased bacterial growth can lead to the clogging of pores and thus alter hydraulic conductivities. Perceptions about the effects on the groundwater ecological system are not available up to now.

Present concepts of hazard and risk assessment are primarily focussing on hot spot pollution. Risk assessment of diffuse pollution effects is usually restricted to effects on human health due to pollutant transfer through the food chain including drinking water and to direct uptake of contaminated soil particles, which is particularly relevant for small children).

Further gaps:

- There is little knowledge about combined effects of different pollutants, indirect effects of pollutants and the influence of other factors on the impact of pollutants

- Not all relevant processes resulting in pollutant transfer between different environmental compartments appear to be sufficiently understood and taken into account (e.g. re-entry of trapped pollutants into natural cycles by excavation of sediments or redistribution and deposition of polluted sediments on land after flood events)

- There is a lack of uniform approaches as well as cheap and reliable procedures to assess and evaluate ecotoxicological effects

- Present approaches assume constant conditions over time

- Present approaches do not or insufficiently consider spatial heterogeneity

- Toxicity (different methods for sample collection), carcinogenicity, bio-availability of pollutants have so far been only marginally considered

- Measurement of medium-term bioavailable fraction of total pollutants which can be assessed (EDTA+ Ammonium acetate buffered extractable methods)

- Hazard assessment of new pollutant or cluster of pollutants entering in the terrestrial ecosystem (e.g. additives such as the distribution of metals having catalysing effects along motorways, anti- knocking)

Various indicators are proposed to monitor polluted soils. Some indicators have been for assessing critical or threshold concentrations. These indicators are not sufficient to indicate the impact of pollutants.

Indicators, which reflect the bio-availability of pollutants are more suitable for assessment of toxicity. Bio-sensors are promising tool to assess the toxicity of pollutant cocktails. Total concentrations of pollutants are of limited value as indicators of actual toxicity.

5.2.4   Measures to reduce, remediate and control diffuse soil and water pollution

5.2.4.1 Diffuse soil pollution

In order to develop an adequate management strategy to manage large-scale diffuse soil pollution, goals have to be set based not only on the pollution and its expected future development but also on the specific functions of the affected soils and their sensitivity. The functions to be considered include the production of food, feed, fruits etc. as well as life supporting ecosystem services of soils. In this context, the filter, buffer and transformation capacity of soils have to be mentioned as essential for groundwater recharge.

Expert Statement

Kees van Beek, KIWA Research, The Netherlands:
Different soils react different upon pollution. For this reason to demonstrate the consequences of pollution a subdivision of soils in geohydrochemical districts is necessary. In order to make this subdivision information about possible interactions of the pollutant and reactive components present in the soil matrix is necessary. This is rather complicated: not always are the possible interactions known, or are data about the presence of reactive soil components available. In particular, the identification of the key-interactions in the various districts is important. The boundaries of districts may vary depending on the presence of the key parameter of relevance for the pollutant under consideration.

Due to measures, the acid atmospheric deposition of sulfur dioxides from power plants has decreased since 1965 considerably. However, up till now the concentration of sulfate in shallow groundwater in wooded areas has not decreased to a comparable extent. Due to measures also the load of the soil by nitrogen from manure has decreased since about 1990. But the concentration of nitrate in shallow groundwater in agricultural areas has not decreased equivalently. This absence of an equivalent decrease in concentration of sulfate and nitrate in shallow groundwater is very disappointing for all actors in both fields: for authorities promulgating measures, for power plant owners and farmers making financial sacrifices and for the public not understanding what is happening

Above mentioned discrepancies point toward a lack of detailed knowledge about the interactions of pollutants and reactive components present in the soil matrix. These interactions are often modeled in a two-dimensional way: concentration of pollutants against for instance constant adsorption capacity, while in the field this capacity may change in time. To overcome above mentioned discrepancies detailed research is necessary in more-dimensional relationships: for instance adsorption capacities varying in time, while for instance also the pH varies independently.

5.2.4.2 Diffuse water pollution

During the last three decades, considerable attempts have been made to develop suitable ways to decrease e.g. diffuse nitrogen and phosphorus loads in waters.

Regulations relating to water protection employ different concepts: protection zones which were issued by water administrations, creation of co-operations between farmers, agricultural administration and water resources managers in water protection zones. Additionally, the Water Framework Directive and the Nitrate Directive of the European Union are supposed to amend emissions to lower levels. In Germany, the recent inventories of water resources managers / water suppliers, however, showed that all these efforts (particularly concerning nitrogen from the agricultural sector) had no success so far.

Various strategies are employed or have been proposed to abate, remediate and control soil and water pollution (Tab. 5.1).

5.2.4.3 Problems of different time constants and delayed responses

Generally, scientific understanding is slow compared to ongoing processes (delayed response). It can take long time periods between the first release of an anthropogenic chemical to the environment and its detection, scientific investigation, and classification as pollutant in different environmental compartments. For instance, the time requirement for transformation of non or slowly degradable organic pollutants and their transfer from soil to water is a big factor of uncertainty for the assessment of pollution responses. Due to a reduction in sulphur emissions since nearly two decades, e.g. topsoils

show today at some places deficiency in sulphur whereas subsoils in contrast show high concentrations of sulphur. Another example is the water tax, which was introduced in some regions in Germany in the late 80ies in order to reduce manure application in groundwater protection zones by paying the farmers for their reduced yields and thus to reduce nitrate emissions to the groundwater. However, the results (no significant reduction of nitrate in groundwater) showed, that a success control of such a measure is maybe not possible within one or decades and that an expected reduction in concentration will become visible in the long-term (some decades) connected with a strict application and control of the measure.

Expert Statement

Claus G. Bannick, Federal Environmental Protection Agency, Berlin, Germany:
Diffuse pollution is a serious threat for soil and water quality at the local, regional and global scale due to the disposal of (non-regulated) materials, soils, waste and due to agricultural activities, atmospheric deposition of pollutants, etc. which in turn can affect large bodies of water. A major concern is the slow but inevitable accumulation of persistent pollutants in top-soils, which is hardly reversible within reasonable periods of time. There is clearly a need for a better understanding of long-term accumulation and fate of pollutants in soils and associated risk of cross-contamination of other environmental compartments. In order to develop and set requirements for a precautionary protection of soil and water, it is necessary to fill these research gaps with knowledge. SOWA with its comprehensive Final Joint Document contributes to decrease current differences in awareness and understanding and clearly identifies scientific research gaps in an integrated approach on soil <u>and</u> water.

The European Commission launched a comprehensive EU soil protection policy - wherein soil is as relevant and important as protection of air and water quality. The needs for an improved soil protection in Europe are clearly addressed by the *Thematic Strategy for Soil Protection,* including different aspects such as soil monitoring, risk assessment, biodiversity and desertification etc… Soil protection is the fundamental prerequisite for successful water protection (groundwater and surface waters).

Various research, development and implementation projects are nowadays carried out in many disciplinary and goal-oriented and nationally separated individual actions without cohesion and without synergy where this might be feasible. This makes it a challenge to arrive at a balanced, transnational, and multi-disciplinarily integrated approach of soil and water use and protection in the wider context of EU. There is the need for a future EU-Soil Protection Directive which has to be well defined and compatible/harmonised with other regulations such as those on fertiliser, waste and building products.

Table 5.1: Strategies/principles to abate, remediate and control soil and water pollution

Please note that not all measures are equally suited to combat or treat large-scale diffuse pollution (see remarks in the table)

Strategy/ principle	Target point	Treatment / Management	Remarks
Preventive hazard avoidance against nutrients and pollutants	Soil	Soil Exchange	Not realistic for large areas
		Immobilisation	Not possible for extended polluted areas, different temporal scale (monitoring is a problem)
		Bioremediation	It is possible in case of low level diffuse pollution
	Soil – Water bodies	Sealing	Can be used for isolated site
		Insulation/encapsulation	Can be used for isolated site
		Rhizofiltration	e.g. keep site all the year green (winter cropping ,use of plants on shore or river banks)
	Soil – Plant	Phyto-rhizo-remediation	Applicable only if long clean up duration is available
		Cultivation restriction	problem of acceptance
	Soil – Animal	Grazing restriction	problem of acceptance
	Plant – Animal	Dilution of fodder	
		Feeding restriction	problem of acceptance
	Soil – Human	Land use restriction	problem of acceptance
	Plant – Animal – Human	Food quality regulations	
	Water - Human	Food quality regulations	
		Water treatments	economic limits
		Diversion or clean up of water sources	Not realistic for large areas
		Bath restrictions	problem of acceptance
	Water bodies	Aeration of water bodies	not in large bodies of water
		Bioremediation	
		Ex-situ treatment	only small bodies of water
Strategy/ principle	**Target point**	**Treatment / Management**	**Remarks**
Curative elimination of hazards	Pollutants inputs	Eliminate sources of pollution	Emission control in heating systems, industrial facilities and traffic; regulation relating to water recycling, run-off water in-filtration, waste water treatment, treatment of bio-wastes etc.
		Reduce inputs of pesticides and optimise fertiliser applications according to crop uptake	Adoption of good agricultural practices, taking into account ground water protection
		Guidelines for the re-use of excavated soil and the use of soil-like materials	Quality control; clean-up of polluted materials by means of bioremediation, soil washing etc.
			Establish trade market excavated soils for re-use
			On principle of end use or composition basis (nutrients, pollutants etc.)
		Guidelines for use of animal and human waste products	Existing treatments are not sufficient for the elimination of residual pharmaceuticals and substances with endocrine-disruptor properties
	Soil – Water bodies	Agricultural equipments and techniques	Avoidance of heavy machines to protect compaction of soil
		Soil pH-increase Increase of adsorption capacity	

Cont. Table 5.1: Strategies/principles to abate, remediate and control soil and water pollution

Strategy/ Principle	Target point	Treatment / Management	Remarks
...Curative elimination of hazards	Soil – Plant	Phytoremediation	It is possible in case of low level diffuse pollution
		Phyto-Rhizoremediation Adaption of crop rotation schemes	
	Soil – Animal	Soil properties and pollution state should be considered in allocating grazing land	
		Fodder quality control regulations	
	Soil – Human	Transfer factors and absorption in intestine	Problems of hazard assessment
	Plant / Animal– Human	Use of food quality labels	Food qulatiy control regulations
	Water – Human	Management of catchment areas	
		Water treatment	
	Water bodies	Quality control guide values for waste water discharges into water streams	
Precautionary principle, avoidance of possible hazards	Emission	Emission control	
		Regulation of inputs	e.g. restriction on the use of Sewage sludge in agriculture
		Regulation on Waste water treatment	
		Laws on Waste management	
		Financial measures	
		Ecological measures such as financial state support for ecological land uses	e.g. avoidance of chemical inputs where ever possible
		Accident cases	
	Land-use	Regulation of landuse with respeect to time and space	
		Separation of protected areas	e.g. groundwater protection zone. Wetlands soil protection zone
		Limitation of agricultural land-use intensity	e.g. establish zones for intensive and extensive farming
		Compensate farmers for yield re-ductions due to ecological land-use restrictions	e.g. contributions for extensively used meadows
		Land management	e.g. crop rotation
	Soil	Soil amelioration and fertility improvement	e.g. phytomelioration, liming, fertilisation, soil organic matter management (side effects need to be considered)
	Re-use of excavated soils and soil like materials	Quality improvement	e.g. consideration of rent
		Soil - market	Quality control is necessary
	Soil – Water bodies	Monitoring, thresholds (precautionary values, trigger values, action values)	
	Soil – Plant	Land use regulations	Appropriate cost neutral and viable regulations
	Soil – Animal	Land use regulations	Appropriate cost neutral and ecological viable regulations
	Plant – Animals	Quality labels for fodder	
	Soil – Human	Aspects should be considered at planning stage of community development and development of recreation sites	
	Plant / Animal – Human	Monitoring	Food quality control
		Food quality regulations	Food quality control
	Water bodies	Monitoring, thresholds	

Cont. Table 5.1: Strategies/principles to abate, remediate and control soil and water pollution

Strategy/ principle	Target point	Treatment / Management	Remarks
Sustainable resource management, Maintainance of resources	General	Indicators to assess the effects of agricultural practices on soil and water quality	Develop specific indicators
		Political actions in agriculture and actions to other political areas	
	Soil	Planning of forest areas	
		Systematic data collection and eva-luation	
		Land use modelling as decision-aid	
		Regional action plans for soil management	Establish soil resource plans
		Remediation, reclamation and re-use of abandoned industrial land (brownfields)	
		Sustainable agricultural and forest management practices	E.g. encourage appropriate crop rotation schemes
	Water bodies	Management at the river basin scale Thresholds, connection to soil protection	

Most relevant scientific questions

5   Management options for large scale soil and water pollution incl. environmental economics / socio-economic issues (=WG5)

- How are the **socio-economic driving forces** (money, education, regulation, administration) influencing management actions (e.g. change to different chemicals, system of crop rotation, cattle unit allowed per acre, no-till, soil–protection as a trade-off)?

- Which possibilities exist for **active management in slowly reacting systems** (time scale: many generations)? Is a decrease of the input (emission reduction) at the source sufficient?

- Is **natural attenuation** an acceptable management option ("passive" management)? How can natural attenuation capacities be quantified and preserved for future generations?

- How can **alternative management options be compared** (apples with oranges)? (evaluation of risk based approaches in decision support systems)?

- Which **long-term goals for soil and water quality** (limit values), compatible with a ecologically, socially and economically sustainable development can be identified? What are the indicators for sustainability?

- Should and how do we interact with the social sciences? Common concept and language! How can **politics and science** interact? What can we learn from the past (nitrate problem)?

6   Conclusions

Successful policies to abate and control diffuse pollution and to manage large-scale polluted soil require an integrated system understanding including socio-economic factors and driving forces. However, the behaviour and fate of diffuse pollution of soils and waters at large scales, the effects of such a large scale pollution on ecosystem functions and life-supporting services is rather poorly understood. In particular, our knowledge of interactions between the different environmental compartments and the anthroposphere needs to be improved. Sectorial solutions for specific problems taking inadequate account of societal factors are not sufficient in the long-term. They can even be contra-productive. Integrative approaches are needed as i.e. the nitrate problem shows. Specific knowledge gaps are:

- There is a lack of adequate quantitative system understanding and pertinent models. For this reason, indirect effects of large-scale pollution are difficult or even impossible to predict.

- Little is known about the quantitative role of preferential and particle-bound transport processes or the role of vegetation on the transfer of metals and other chemicals in the root zone on field to river basin scales.

- Knowledge about the effects of mixed pollution ("cocktail pollution") is sparse.

- Many pathways of pollutant transport and transformation in the environment have not yet been sufficiently identified or quantified, for example pollutant transfer from soil to plant due to re-suspension of contaminated soils by wind and rain-water splash or the uptake of pollutants by humans and animals through dermal soil contact.

- Little is known about the effects of climate and land use changes on soil functions and potentials at a large scale.

- Despite much progress in recent years, there is still considerable lack of uniform approaches and standardised procedures to assess and evaluate ecotoxicological effects of diffuse soil and water pollution.

- Emerging techniques for a gentle remediation of already polluted agricultural soils, e.g. plant-based risk-reduction, clean-up and site-stabilisation schemes, are still not operational at the field scale.

- There is a great need for theoretical knowledge how stakeholder decisions and actions affecting soil and water quality can be influenced to achieve the goals of pollution reduction and sustainable land-use and how respective policies can be implemented in practice.

Given these gaps and the potential risks arising from the accumulation of large-scale diffuse pollution in soils and water bodies, the following tasks need to be addressed urgently in order to cope effectively and in a sustainable way with this challenging problem:

- Investigation of driving forces, magnitude and dynamics of diffuse pollutant fluxes at field, farm, regional and larger scales between soil, water, other environmental compartments and the anthroposphere, in particular agriculture: methods of assessment (such as mapping and mass flux analysis), controlling factors, possibilities for active management.

- Evaluation of long-term effects of diffuse soil and water pollution on life-supporting eco-system services and goods, climate, biodiversity, and health, including pathway-specific evaluation of risks due to pollutant transfer from soil and water into food chains and other exposure pathways.

- Identification of consistent long-term goals for soil and water quality, compatible with a ecologically, socially and economically sustainable development.

- Design of adequate strategies (e.g. in spatial and land use planning) and instruments (policies, regulations, management procedures, technical processes etc.) to prevent further diffuse soil and water pollution.

- Development of techniques to eliminate or control risks arising from existing diffuse pollution, compatible with the goals of sustainable development: studies on natural attenuation, potential for stabilisation, possible ways for large-scale amelioration of low-to-medium level polluted soils and waters, in particular by using "green" techniques such as phytoremediation.

- Harmonisation of methods and procedures to survey and monitor diffuse soil and water pollution, to assess hazards and risks emanating from such pollution, and regulations regarding present and future diffuse soil and water pollution.

- Improvement of the knowledge transfer between the various actors and stakeholders (e.g. scientists, farmers, administrators, planners, politicians, general public).

To accomplish these tasks, it is important to take adequate account of the specific difficulties arising from the diffuse, long-term and – due to the involved uncertainties – ill-defined nature of the problem.

First of all, the spatial heterogeneity of soils and aquifers at the scale of interest must be considered. Effective control of diffuse pollution requires coordination with land-use planning and thus should be based on policies and action plans which take account of the uneven spatial distributions of as well as the interrelationships between the various potential uses, ecosystem functions and vulnerabilities of the soil and water resources to be managed.

Then, the disparity of time scales must be taken into account. Because of the low rate of accumulation, the delay until adverse effects become manifest and the even longer times – in certain cases this may take generations – until counter-measures become effective, it is necessary to intervene early against diffuse pollution, long before the pollution exceeds thresholds above which negative impacts on ecosystem functions become manifest. Not only the time constants of the biophysical system need to be considered, but also of the socio-economic processes involved.

Finally, historical experience shows that human impacts on the environment always include risks which nobody has been able to think about in the beginning. To cope with such uncertainty, basic strategies based on the precautionary principle must be developed and established in a politically responsible approach to maintain the multi-functionality of soils and the quality of waters.

Expert Statement

Stefan Siebert, University of Frankfurt, Germany:
The actual SOWA-report gives a good overview on problems related to large-scale soil and water pollution and addresses the main scientific issues. To my mind it will be a main scientific challenge to quantify indirect effects of human-induced environmental pollution and environmental changes. One example is the recently reported damage of German forest ecosystems as consequence of climatic effects, air- and soil pollution. Another example is the reported change of freshwater- and marine ecosystems as consequence of dam construction and nutrient intakes from industry, agriculture and sewage. Those examples have in common that reported changes cannot be attributed to a single reason and that large scale phenomena have to be considered. Although the involved processes are usually well known the effects of possible interactions are often very uncertain. Therefore more system-oriented approaches may be required. A major target should be to reduce the existing uncertainty in global – or regional change research to give more scientific support for necessary decisions of policy makers and to provide a more rational basis for the public discussion of appropriate measures.

ANNEX

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(Joint Danube Survey, hydrocarbons, PAH, linear alkylbenzene sulfonates, musk compounds, alkylphenol ethoxylates, endocrine modulators, hormones, pharmaceuticals, polybromated flame retardants)

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Switzerland

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A2 Internet addresses of authorities of European Countries which responded to the inquiry (chapter 4.3)

Austria

http://umweltbundesamt.at

Germany

http://www.umweltbundesamt.de/

Netherlands

http://www.rivm.nl/en/

Sweden

http://www.internat.naturvardsverket.se/

Switzerland

BUWAL, NAQUA, NABEL, Umweltbeobachtung

http://www.umwelt-schweiz.ch/buwal/de/

Swiss National Soil Monitoring

www.nabo.admin.ch

Soil Monitoring & Forest Ecology

http://www.wsl.ch/forest/soil/monitoring-de.ehtml

United Kingdom

http://www.defra.gov.uk/

http://www.environment-agency.gov.uk/

Contaminated Land Exposure Assessment:

http://www.environment-agency.gov.uk/subjects/landquality/113813/672771/?version=1&lang=_e

http://www.defra.gov.uk/environment/land/contaminated/index.htm

Diffuse sources of water pollution, protection of water resources:

http://www.defra.gov.uk/environment/water/quality/diffuse/non-agri/index.htm

http://www.defra.gov.uk/environment/water/quality/diffuse/non-agri/research/index.htm

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A3 Tables

Table A3.1: List of priority substances in the field of water policy

Priority hazardous substances	Priority hazardous substances under review	Priority substances not proposed as priority hazardous substances
PBDEs (only penta) Cadmium Mercury C_{10}-C_{13} chloroalkanes Hexachlorobenzene Hexachlorocyclohexane Tributhyltin compounds Hexachlorobutadiene Nonylphenols PAH Pentachlorobenzene	Anthracene Atrazine Chlorpyrifos Di(2-eththexyl)phthalate (DEHP) Endosulfan Lead Naphthalene Octylphenols Pentachlorophenol Trichlorobenzenes Trifuralin	Alachlor Benzene Chlorfenvinphos Dichloromethane 1,2-Dichloroethane Diuron Isoproturon Nickel Simazine Trichloromethane
Subject to phase-out or under consideration for phase–out (or severe restriction) on the international level	Shows properties similar to those identified as "Priority Hazardous" (group 1). Subject to a review for identification as possible priority hazardous substances by 31 December 2003	Do not fulfil the criteria for being "toxic, persistent and likely to bio-accumulate". Classified as dangerous. Subject to emission controls and quality standards

Table A3.2: Toxic Equivalent Factors for human exposure established by the WHO (WHO-TEFs) for dioxins and dioxin-like PCBs. Relative potencies (REPs) schemes for PAHs and for some BFRs.

PCDD	TEF	PCDF	TEF	PCB	TEF	PAH *	REP (a)	REP (b)	REP (c)	BFRs	REP
2,3,7,8-TCDD	**1**	**2,3,7,8-TCDF**	**0.1**	*Non-ortho*		BkF	0.00478	0.05	0.00029	*PBDEs*	
12,3,7,8-PeCDD	**1**	**12,3,7,8-PeCDF**	**0.05**	**PCB#81**	**0.0005**	BAP	0.000354	0.00001	0.0003	BDE-47	7.1×10^{-7}
123478-HxCDD	**0.1**	**23478-PeCDF**	**0.5**	**PCB#77**	**0.0005**	BbF	0.00253		0.00038	BDE-77	0.0032
123678-HxCDD	**0.1**	**123478-HxCDF**	**0.1**	**PCB#126**	**0.1**	Chr	0.0002	0.01		BDE-99	5.9×10^{-6}
12,3,7,89-HxCDD	**0.1**	**123678-HxCDF**	**0.1**	**PCB#169**	**0.01**	BA	0.000025	0.00001	0.000027	BDE-100	2.4×10^{-5}
1234678-HpCDD	**0.01**	**234678-HxCDF**	**0.1**	*Mono-ortho*		IdP	0.0011		0.000086	BDE-119	3.5×10^{-5}
OCDD	0.0001	**12,3,7,89-HxCDF**	**0.1**	**PCB#105**	**0.0001**	DBA	0.00203	0.05	0.000078	BDE-126	0.0024
		1234678-HpCDF	**0.01**	**PCB#114**	**0.0005**	**Ant**		0.0001		BDE-153	4.3×10^{-6}
		1234789-HpCDF	**0.01**	**PCB#118**	**0.0001**						
		OCDF	0.0001	**PCB#123**	**0.0001**					*PBBs*	
				PCB#156	**0.0005**					PBB-77	0.08
				PCB#157	**0.0005**					PBB-169	0.021
				PCB#167	**0.00001**						
				PCB#189	**0.0001**					*PBDDs*	
										2378-TBDD	0.65
										1378-TBDD	0.013
										12378-PBDD	0.30
										PBDFs	
										2378-TBDF	0.7
										12378-PeBDF	0.5
										23478-PeBDF	0.21
										123478-HxBDF	0.002

* BkF = Benzo[k]fluoranthene; BAP = Benzo[a]pyrene; BbF = Benzo[b]fluoranthene; Chr = Chrysene; BA = Benzo[a]anthracene; IdP = Indeno[1,2,3-c,d]pyrene; DBA = Dibenzo[a,h]anthracene; Ant = Anthracene

Table A3.3: Summary of the state of soil monitoring in European countries (based on EEA Technical Report 61; EEA 2001a)

Country	Forest soil monitoring	National soil pollution monitoring network	Year of establishment	Soil erosion	Organic pollutants	Radionuclides	Trace elements analysis		Pesticides
							Trace element	**Extraction**	
Austria	ICP forest	4 km	first region in 1986	●	●	●	large spectrum	agricultural aqua regia forest mixture of HNO_3 and $HClO_4$	
Belgium	ICP forest	non-existent							
Czech Rep.	ICP forest	non-existent					Cd, Co, Cr, Cu, Ni, Pb, Zn, Hg		
Denmark	ICP forest	7 km	1998	●			Cd, Cr, Cu, Pb, Hg, Ni, Zn		●
Estonia	ICP forest	not regular grid	being organised				Cd, Cr, Cu, Hg, Ni, Pb, Zn	HF / HNO_3 / $HClO_4$ (Cd, Cu, Zn), X-ray-fluorescence (Pb), gas analyser (Hg) and spectral analysis (Cr, Ni).	
Finland	ICP forest	non-regular grid	1974	● southern part			Cd, Pb, Cr, Cu, Mn, Mo, Ni, Pb, Zn	aqua regia	
France	ICP forest	repre-sentative sites	1968: soil survey 1990: soil information system	●		●	Cd, Cr, Cu, Mn, Ni, Pb, Zn, in some areas also As, Co, Hg, Se, Ti	aqua regia and mixture of HNO_3/ $HClO_4$	
Germany	ICP forest	organi-sation on the regional scale	1980/1997: dependent on the region	●	●	●	large spectrum (dependent on the region)	different methods used in regions transferred to aqua regia basis using regression functions	●

Cont. of Table A3.3:

	National soil monitoring activities								
Country	**Forest soil monitoring**	**National soil pollution monitoring network**	**Year of establishment**	**Soil erosion**	**Organic pollutants**	**Radionuclides**	**Trace elements analysis**		**Pesticides**
							Trace element	**Extraction**	
Greece	ICP forest	non-existent		● in the frame of CORINE					
Hungary	ICP forest	repre-sentative sites	1992		in some points				in some points
Ireland	ICP forest	10 km; (up to now only 25% of territory)	1996		●		Cu, Mo, Mn, Zn, As, Cd, Cr, Co, Pb, Hg, Ni, Se	mixture (HF/ HNO_3 / HCl / H_2O	
Italy	ICP forest	non-existent							
Latvia	ICP forest	non-regular grid	1992	●			Pb, Cd, Ni, Cr, Cu, Zn, Mn		
Lithuania	ICP forest	non-existent		●					
Netherlands	ICP forest	non-existent on a national scale	in some provinces since 1991		●		large spectrum	different extraction methods	●
Norway	ICP forest	agricultural, non-regular (9 km for forest areas)	1992	●			large spectrum	1 M NH_4NO_3	partially only by leaching
Poland	ICP forest	non-regular grid	1992	●	●	●	Mn, Cd, Cu,Cr, Ni, Pb, Zn, Co, V, Li, Be, Ba, Sr, La	aqua regia	
Portugal	ICP forest	non-existent		partially moni-tored					
Slovenia	ICP forest	4,2 or 1 km	2000		●		Cd, Pb, Cr,Cu, Ni, Pb, Zn, Hg		●

Cont. of Table A3.3:

Country	Forest soil monitoring	National soil pollution monitoring network	Year of establishment	Soil erosion	Organic pollutants	Radionuclides	Trace elements analysis		Pesticides
							Trace element	Extraction	
Slovakia		1/14 ha	1992	not at every point	●	●	large spectrum	mixture of HF / HNO$_3$ (Cd, Cu, Ni, Pb, Zn) or Na$_2$O$_2$ (Cr) or by AMA (Hg)	
Spain	ICP forest	non-existent		some national monito-ring programs					
Sweden	ICP forest	5 km in Southern part, 15 km in Northern part	1993				large spectrum		
UK	ICP forest	5 km grid	1979				Cd,Co, Cr, Cu, Pb, Mn, Ni, Zn since 1994 also V, As, Hg, Se		
Switzerland	ICP forest	NABO	monitoring organised since 1986	●	not in every Canton		Cd, Co, Cr, Cu, Hg, Ni, Pb, Zn, F	2 M HNO$_3$	

Table A3.4.1: Overview over standardised sampling guidances

number	title	state
ISO 10381	Soil Quality: Sampling	
BS ISO 10381-1: 2002: Part 1	Guidance on the design of sampling programs	working document
BS ISO 10381-2: 2002: Part 2	Guidance on sampling techniques	working document
BS ISO 10381-3: 2001: Part 3	Guidance on safety	working document
ISO FDIS 10381-4: Part 4	Guidance on the procedure for investigation of natural, nearly natural and cultivated sites	final draft international standard
ISO DIS 10381-5: Part 5	Guidance on the investigation of soil contamination of urban and industrial sites	draft international standard
ISO 10381-6: 1993: Part 6	Guidance on the collection, handling and storage of soil for the assessment of aerobic microbial processes in the laboratory	standard
ISO CD 10381-7.2: Part 7	Sampling of soil gas	committee draft
ISO WD 10381-8: Part 8	Guidance on the sampling of stockpiles	working draft
ISO WD 15185	Soil Quality: Sampling: Specification of soil augering/drilling apparatus	cancelled in the stage of working draft mainly because it is too broad a subject.
ISO WD 15185	Soil quality -- Extraction of trace elements soluble in aqua regia	working draft

Table A3.4.2: Overview over analytical methods (organic compounds)

number	title	state
BS ISO 14507: 2002	Pretreatment of samples for determination of organic contaminants	standard
ISO 10382	Determination of organochlorine pesticides and polychlorinated biphenyls - Gas-chromatographic method with electron capture detection	standard
ISO TR 11046: 1994	Determination of mineral oil content -- Method by infrared spectrometry and gas chromatographic method	standard
ISO 13877: 1998	Determination of polynuclear aromatic hydrocarbons -- Method using high - performance liquid chromatography	standard
BS ISO 15009: 2002	Gas chromatographic determination of the content of volatile aromatic hydrocarbons, naphthalene and volatile halogenated hydrocarbons -- Purge-and-trap method with thermal desorption	standard
ISO FDIS 14154	Determination of phenols and chlorophenols: Gas-chromatographic method with electron-capture detection	final draft international standard
BS ISO 14507: 2002	Pretreatment of samples for determination of organic contaminants	standard
ISO DIS 18287	Determination of polycylic aromatic hydrocarbons (PAH): Gas chromatographic method with mass spectrometric detection	draft international standard
ISO 10693: 1995	Determination of organic and total carbon after dry combustion (elementary analysis)	standard
ISO 14235: 1998	Determination of organic carbon by sulfochromic oxidation	standard
ISO 16703	Determination of content of hydrocarbons in the range C_{10} to C_{40} by gas chromatography	standard

Table A3.4.3: Overview over analytical methods (inorganic compounds)

number	title	state
ISO 11464: 1994	Pretreatment of samples for physico-chemical	standard
ISO 11047:1998	Determination of cadmium, chromium, cobalt, copper, lead, manganese, nickel and zinc -- Flame and electro-thermal atomic absorption spectrometric methods	standard
ISO 11466: 1995:	Extraction of trace elements soluble in aqua regia	standard
ISO 11048:1995	Determination of water-soluble and acid-soluble sulphate	standard
ISO 15178:2000	Determination of total sulphur by dry combustion	standard
ISO 14869-1: 2001	Determination of total trace element content: Part 1: Digestion with hydrofluoric and perchloric acids	standard
BS ISO 14869-2: 2002	Dissolution for the determination of total element content: Part 2: Dissolution by alkaline fusion.	standard
ISO 14870: 2000	Extraction of trace elements by buffered DTPA solution	standard
ISO 16772	Determination of mercury in aqua regia soil extracts	standard
ISO DIS 20279	Determination of thallium: Method by extraction and determination by electro-thermal atomic absorption spectrometry	draft international standard
ISO DIS 20280	Determination of arsenic, antimony and selenium: Method by extraction in aqua regia and atomic absorption spectrometry	draft international standard
ISO 11262	Determination of cyanide	standard
ISO 17380	Photometric determination of total cyanide and free cyanide content: Method by continuous flow analysis	standard
ISO NP 11264	Determination of herbicides: Method using HPLC with UV detection	new proposal
ISO 10390: 1994	Determination of pH	standard
ISO 10693: 1995	Determination of carbonate content: Volumetric method	standard
ISO 11260: 1994	Determination of effective cation exchange capacity and base saturation level using barium chloride solution	standard
ISO 11261: 1995	Determination of total nitrogen: Modified Kjeldahl method	standard
ISO 11263: 1994	Determination of phosphorus: Spectrometric determination of phosphorus soluble in sodium hydrogen carbonate solution	standard
ISO 11265: 1994	Determination of the specific electrical conductivity	standard
BS ISO 11271: 2002	Determination of redox potential: Field method	standard
ISO 11465: 1993	Determination of dry matter and water content on a mass basis: Gravimetric method	standard
ISO 13536: 1995	Determination of the potential cation exchange capacity and exchangeable cations using barium chloride solution buffered at pH = 8.1	standard
ISO 13878: 1998	Determination of total nitrogen content by dry combustion ("elemental analysis")	standard
ISO 14254	Determination of exchangeable acidity by barium chloride extract	standard

Cont. of Table A3.4.3: Overview over analytical methods (inorganic compounds)

ISO 14255: 1988	Determination of nitrate nitrogen, ammonium nitrogen and total soluble nitrogen in air-dry soils using calcium chloride solution as extractant	standard
ISO14256-1	Determination of nitrate, nitrite and ammonium in field moist soils by extraction with potassium chloride solution: Part 1: Manual method	standard
ISO CD 14256-2:	Determination of nitrate, nitrite and ammonium in field moist soils by extraction with potassium chloride solution: Part 2: Automated method	committee draft
ISO FDIS 16720:	Determination of dry residue by freezing	final draft international standard
ISO CD 19492:	Leaching procedures for subsequent chemical and ecotoxical testing of soil and soil materials: Influence of pH on leaching with initial acid/base addition	committee draft
ISO NP 20923:	Determination of potential cation exchnage capacity for clay-rich soils and soil materials	new proposal

Table A3.4.4: Overview over methods on soil and site assessment (organic compounds)

number	title	state
ISO DIS 14015	Environmental management: Environmental assessment of sites and organisations	draft international standard
BS ISO 15175: 2004	Characterisation of soil related to groundwater protection	standard
BS ISO 15176: 2002	Characterisation of excavated soil and other soil materials intended for re-use	standard
BS ISO 15799: 2003	Guidance on the ecotoxological characterization of soils and soil materials	standard
ISO FDIS 15800	Characterization of soil with respect to human exposure	final draft international standard
ISO 16133	Guidance on the establishment and maintenance of monitoring sites	standard
ISO DIS 19258	Guidance on the determination of background values	draft international standard
ISO CD 17924	Bioavailability of metals in contaminated soil: Physiologically based extraction method	committee draft
ISO DIS 21268-1	Leaching procedures for subsequent chemical and ecotoxilogical testing of soil and soil materials. Part 1. Batch test using a liquid to solid ratio of 2 l/kg dry matter	draft international standard
ISO AWI 21268-2	Leaching procedures for subsequent chemical and ecotoxilogical testing of soil and soil materials. Part 2. Batch test using a liquid to solid ratio of 10 l/kg dry matter	approved work item
ISO DIS 21268-3	Leaching procedures for subsequent chemical and ecotoxilogical testing of soil and soil materials. Part 3. Up-flow percolation test	draft international standard

Why is research for integrated soil and water protection against diffuse pollution necessary?

Each year, anthropogenic compounds are released to the environment, transported over short and long distances from local to the global scale. Scientists are surprised by how quickly some substances spread towards remote areas and how they suddenly appear in soil, water, animals, and humans. Diffuse pollution is occurring globally including urban sprawl as well as rural regions. For instance, persistent organic compounds such as flame retardants widely used in products of daily life (i.e. furniture, computers) are found already in wildlife (seals, polar bears) and humans of the artic region. Some heavy metals occur in soils of urban areas sometimes already at levels higher than the precautionary limits. Elevated concentrations of carcinogenic hydrocarbons from incomplete combustion processes (heating, traffic) are not only found in highly industrialised regions but also in forest soils in rural areas. Due to their chemical properties, such persistent compounds gradually accumulate in soils even if the input rates are low. Polluted soils will eventually loose their important function as filter and buffer in the water cycle. Soils are the key element in the water cycle determining the quality of groundwater, surface waters and finally drinking water.

Until today, this close interaction of soil and water has not been considered in a holistic, integrative way. Scientific disciplines often still see soil and water as separate bodies and a sufficient understanding of the functioning of the soil and water as an integrated system is missing. Thus, research on integrated soil and water protection is necessary for a better scientific understanding of the fate of new chemical compounds, transport and degradation processes and their spatiotemporal variability, impact of various scales as well as the development of tools and the prediction of accumulation trends of compounds in soil and groundwater. An improved understanding is the prerequisite for the mitigation of the impacts of diffuse pollution as well as for the development of adequate management strategies for soil and water pollution in ecosystems at different scales.

Therefore, an European interdisciplinary consortium of scientists (SOWA) identified the main research needs in integrated soil and water protection which have to be addressed in future towards integrated soil and water protection against diffuse pollution.

Integrated Soil and Water Protection:
Risks from Diffuse Pollution (SOWA)
Contact the Co-ordinator:
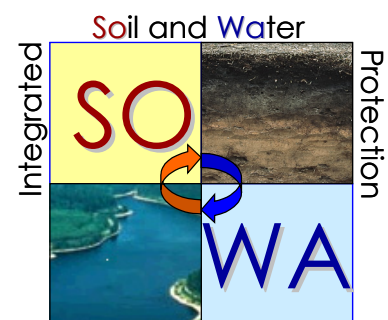Dr. Dietrich Halm, Prof. Dr. Peter Grathwohl
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Soil and Water

Integrated

Protection

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Risks from Diffuse Pollution