Project No. SN-01/19

IOPSIM

Full Title of Research Project

(Im)mobilization of organic pollutants by soil constituents in the soil/ground water system – Strategies for innovative management.

Final Research Report

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Abstract

In industrialised countries, soil and groundwater contamination by various forms of harmful substances is a contemporary problem in this highly industrialized age. Therefore, minimising health risks and impacts on the environment, caused by the contaminants, is urgently needed, also for fitting the land use requirements and to ensure a permissible land use for the future generations.

In the last years, research was successfully performed and has increased our knowledge about the behavior of organic chemical substances in the soil-water system and the factors that control their behavior. This knowledge is of primary importance to (i) predict the fate and potential risk, (ii) ensure public safety and environmental protection, and (iii) enable rational decision-making for the development of management strategies, suitable tools and effective techniques.

In this document, the state of the art regarding the main mechanisms, processes and factors governing the fate and behavior of organic contaminants in the soil-ground water system is reviewed.

In this area, an enormous amount of literature exists, mostly focusing on pesticides, because annually large quantities are applied in agriculture each year. At present, less is known about the fate of pharmaceuticals e.g. antibiotics and personal care products (PCP) in the soil and ground water system.

The study aims to report and discuss the progress that has been made in these particular areas in the last few years. Current knowledge is brought together and reviewed,,generally related to organic contaminants in soils and sedimentary environments like groundwater aquifers. Reviews and the most important primary publications are considered. The scope is to provide useful and precise information for end-users and support their work in the field of organic pollutants in the environment and to stimulate the development of new techniques for a sustainable management.

Summary

The behavior of organic contaminants in soils is generally governed by a variety of complex dynamic physical, chemical and biological processes, including sorption–desorption, volatilization, chemical and biological degradation, uptake by plants, run-off, and leaching. These processes directly control the transport of contaminants within the soil and their transfer from the soil to water, air or food. The relative importance of these processes varies with the chemical nature of the contaminant and the properties of the soil. Both the direction and rate of these processes depend on the chemical nature of the organic contaminant and the chemical, biological, and hydraulic properties of the soil. Some organic contaminants are degraded in the soil within a certain time. On the other hand some degrade only slowly or are sequestered within soil particles by being inaccessible for microbial degradation. Persistence in soils increases the potential for environmental consequences. Mobility in soil environments is a key factor in assessing the environmental risk. Some compounds are strongly adsorbed on the surface of soil particles and remain in the soil. Compounds interacting weakly or not at all with soil surfaces will be leached together with the soil solution and have the potential for contaminating surface or ground water reservoirs far from the point of getting into the soil. Clays, oxides and organic matter are the primary constituents in soils responsible for the sorption of organic contaminants. Organic matter has a high affinity for many nonpolar compounds and typically dominates sorption if the content is >3%. For soils and sediments with low organic matter content clay minerals have a decisive role in sorption processes.

Here the state-of-the-art with respect to the environmental fate of organic contaminants and different remediation techniques is reported after one year of literature research. Influences of different soil and environmental characteristics on organic contaminants behavior in soil and groundwater are highlighted and summarized in this review. Also, results of literature research on some current and emerging organic pollutants in form of case studies are presented. Based on this literature research, knowledge gaps were defined as well as directions for future investigations. Moreover, recommendations for the improvement of risk management were developed after intensive discussion with end-users and presented in the form of precise information. Dissemination of important project results by different publications is under way/or are planned for the near future.

Acknowledgments

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Use of grant

The grants were used to support financially the work of collaborating scientists:

BOKU: Gorana Rampazzo Todorovic worked as a research and coordination assistant

IfBk: Jochen Walsch worked as a student research assistant and prepared his Diploma thesis within the project and finalized it as a Dipl.-Geow.

UBA-A: Alexandra Freudenschuß, Yvonne Spira and Harald Loishandl-Weisz worked for the project

1 Background/need/adequateness of the work made

Within the scope of this project "emerging pollutants" are understood as substances that are expected to cause adverse effects in humans, wildlife and the environment. These are not necessarily new chemicals but less is known about (eco)toxicity and potential impacts on human health and environment.

For instance, flame retardants e.g. pentabromobiphenylether, 4-nonylphenol, C_{10}-C_{13} chloroalkanes and the plasticizer di(2-ethylhexyl)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. In October 2008 the European Chemicals Agency (ECHA) identified in a first step 15 substances to be of very high concern (including e.g. plasticizers Dibutyl phthalate (DBP), di(2-ethylhexyl)phthalate (DEHP) or flame retardant C_{10}-C_{13} chloroalkanes). Furthermore human and veterinary antibiotics such as tetracyclines or sulfonamides or active hormonal substances (natural hormones are active at levels of ng/l) are being widely used. For many of the occurring emerging contaminants, risk assessments as well as exposure and (eco)toxicological data are only limited or not available. Therefore it is difficult to predict the effects they may have on humans, terrestrial and aquatic organisms, and ecosystems, especially if long term exposure occurs. In this respect the budgets (sources, entry routes, and fate) for environmental pollutants are also of great importance.

A huge amount of literature exists on occurrence of specific groups of organic contaminants in the environment. In the past research priorities have focused on priority pollutants, such as persistent organic pollutants (POPs), pesticides, toxic metals, radionuclides. Recently, the attention of the scientific community focused on emerging contaminants. Emerging contaminants can be defined as pollutants that are currently not included in routine monitoring programmes at the European level and which may be candidates for future regulation, depending on research on their (eco)toxicity, potential health effects and public perception and on monitoring data regarding their occurrence in the various environmental compartments. Therefore, a task within this project was to identify and select substances which potentially will gain relevance in the interaction of the soil – ground/surface-water system. The major sources of environmentally relevant emerging contaminants are on the one hand wastewater treatment plants effluents, terrestrial run-offs (e.g. agricultural land) including atmospheric deposition and local contaminated sites. A selection of several emerging contaminants in the environment is shown in Table 1.

Table 1: Selection of emerging pollutants in the environment (Source: SOWA – report 2005, modified) http://www.uni-tuebingen.de/sowa/download/SOWA_Final_Joint_Document_V2_final.pdf)

Pharmaceuticals	**Examples**
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
b-blockers	Metoprolol, propanolol, timolol
X-ray contrasts	Iopromide, iopamidol, diatrizoate
Endocrine disruptors	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)
Energetic compounds	Trinitrotouluol (TNT), Nitroamine

SOWA – report 2005: http://www.uni-tuebingen.de/sowa/download/SOWA_Final_Joint_Document_V2_final.pdf

At international Level the ‚Protocol on Persistent Organic Pollutants' (1998) of UN-ECE as well as the Stockholm-Convention (UNEP 2001) aim to reduce the impact of POPs by prohibition, restriction or mandatory directives.

The **Stockholm Convention** is a global treaty that entered into force in May 2004 to protect human health and the environment from persistent organic pollutants (POPs). By definition POPs are chemicals that remain intact in the environment for long periods, become widely distributed geographically, accumulate in the fatty tissue of living organisms and are toxic to humans and wildlife. In implementing the Convention, Governments will take national measures to comply with the requirements of the Convention. Currently the Convention lists 12 POPs in Annex A, B or C ("dirty dozen"). The POP Review Committee (POPRC) has the mandate to deal with the procedural and technical aspect to identify and propose new substances for amendment of the POPs list (Annexes). The procedure to list a new POP is divided into 3 stages (screening, risk profile and risk management):

Screening (1.level):

- Hexabromocyclododecane (bending)
- Endosulfan (endorsed)

Risk profiles (2. level):

- short-chained chlorinated paraffins (SCCPs) (bending)

Risk management evaluation (3. level):

- Lindane (endorsed)
- alpha and beta hexachlorocyclohexane (HCH) (endorsed)

- commercial octabromodiphenylether (c-octaBDE) (endorsed)
- Chlordecone (endorsed)
- Pentachlorobenzene (PCB) (endorsed)
- Hexabrombiphenyl (HBB) (endorsed)
- commercial pentabromodiphenylether (c-pentaBDE) (endorsed)
- PFOS – perfluorooctane sulfonates and it's salts and PFOS fluoride (PFOSF) (endorsed)

The **Convention on Long-range Transboundary Air Pollution of the United Nations Economic Commission for Europe (UNECE)** has addressed some of the major environmental problems of the UN ECE region through scientific collaboration and policy negotiation. The Convention has been extended by eight protocols; one on POPs, which identifies specific measures to be taken by Parties to cut their emissions of air pollutants.

The POPs Protocol focuses on a list of 16 substances - eleven pesticides, two industrial chemicals and three by-products/contaminants. The objective is to eliminate any discharges, emissions and losses of POPs. The Protocol bans the production and use of some products outright (aldrin, chlordane, chlordecone, dieldrin, endrin, hexabromobiphenyl, mirex and toxaphene). Others are scheduled for elimination at a later stage (Dichlodiphenyltrichlorethan (DDT), heptachlor, hexaclorobenzene, PCBs). Finally, the Protocol severely restricts the use of DDT, HCH (including lindane) and PCBs. The Protocol includes provisions for dealing with the wastes of products that will be banned. It also obliges Parties to reduce their emissions of dioxins, furans, polycyclic aromatic hydrocarbons (PAHs) and hexachlorbenzol (HCB) below their levels in 1990 (or an alternative year between 1985 and 1995). For the incineration of municipal, hazardous and medical waste, it lays down specific limit values. The inclusion of further substances is also intended:

Substances under discussion for nomination:

- Dicofol
- Endosulfan
- Pentachlorphenol
- Trifluralin
- HBCD-Hexachlorbutadien

Suggested substances:

- PFOS - perfluorooctane sulfonates
- C-PentaBDE - pentabromodiphenylether
- C-octaBDE - octabromdiphenylether
- PCN – polychlorinated Naphthalens
- HCBD – Hexachlorbutadien
- SCCPs – short-chained chlorinated paraffins

As a daughter directive of the Water Framework Directive the **Groundwater Directive 2006/118/EC** specifies measures to ensure groundwater quality:

- Assessing groundwater chemical status:

Pollutant	**Quality standards**
Active substances in pesticides, including their relevant metabolites, degradation and reaction products	0,1 µg/l
	0,5 µg/l (total)

- Minimum list of pollutants and their indicators for which MS have to establish threshold values:

Arsenic	Ammonium	Trichloroethylene
Cadmium	Chloride	Tetrachloroethylene
Lead	Sulphate	Conductivity
Mercury		

Moreover, there is a broader concern, not to relate only on individual chemical properties of a specific substance. Human and eco-system exposure tend not to be limited to just one particular compound or group of compounds, but rather to a mixture of micro-organic contaminants causing synergistic effects which are still unknown.

On the other hand, the number of chemicals in our environment is rapidly growing and until now, only a small portion of these substances were properly investigated (Wackett, 2004).

Most discreet organic chemicals are measurable by sophisticated instrumental methods, and procedures are available to assess exposure risks in many cases. However, often insufficient experimental toxicology data are available to perform detailed risk assessments (Asano & Cotruvo, 2004). The most relevant analytical methods for determining pesticides and their transformation products in soils were reviewed from Andreu & Pico (2004). In addition, O`Connor & Aga (2007) discussed in a review several strategies for sample preparation, extraction, clean-up and analysis of tetracyclines and their transformation products in soil, with the aim to facilitate future environmental fate studies, and to challenge analytical chemists to develop the necessary tools to allow a complete risk assessment of other pharmaceutical contaminants in the environment. Screening techniques like biologically based assays (BBAs) may provide major advantages by estimating the total estrogenic effects of many estrogenic endocrine disrupting compounds (e-EDCs) in the environment and may potentially be adapted for field portable biologically directed sampling and analyses (Campbell *et al., 2006)*. In this review available BBAs used to measure estrogenic e-EDCs in the environmental samples and also present results relating to fate and transport of e-EDCs are summarized. Several of these issues were also covered by Ying *et al.* (2004) in a literature review performed within the frame of the ”Australian Water Conservation and Reuse Research Program” on trace organic constituents in recycled water in Australia. In this study many chemicals and naturally produced hormones contained in sewage have been detected at very low concentrations. Environmental and health considerations, awareness in risk management demands and research to fill current knowledge gaps were addressed in this study under the categories; sources, fate, receptors and risk assessment.

There is also need for more investigation of environmental fate of the transformation products of the organic contaminants. These metabolites can comprise an extremely complex mixture (Fig. 1), sometimes are more toxic and persistent than the parent molecules and can show different environmental behavior than parent material.

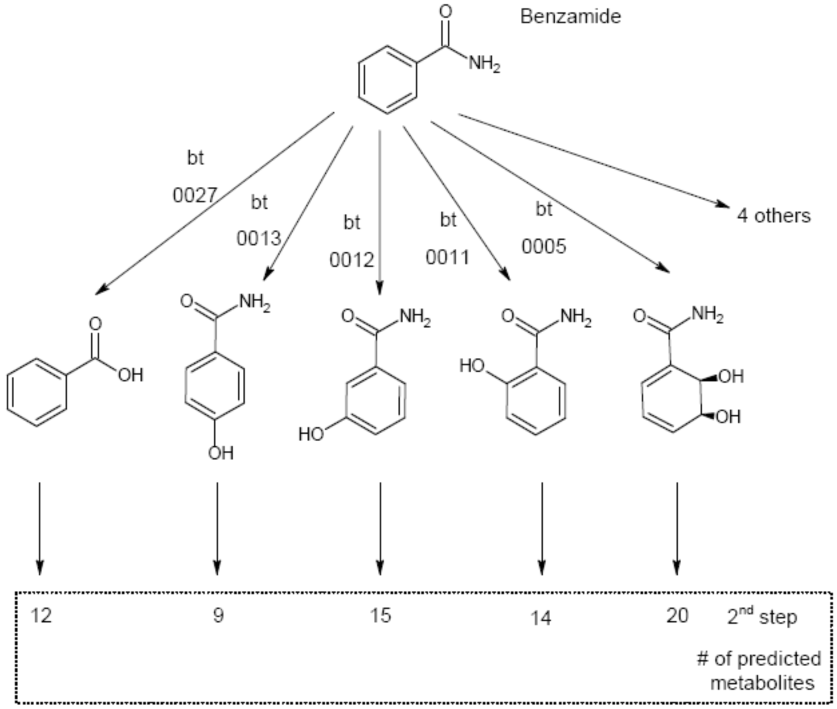


Figure 1: Degradation of a single benzamide molecule (Wackett, 2004)

For a better risk assessment, existence of a comprehensive contaminant database in a format that allows direct linking to software applications is necessary (risk assessment systems). This database should contain:

- General information's: common and chemical names, chemical group, formula, structures

- Physico-chemical data: solubility, vapor pressure, density, dissociation constants, melting point, degradation products

- Environmental fate data: octanol-water partition constant (Kow), Henry's law constant, degradation rates, Freundlich sorption coefficient (Kf), organic-carbon sorption constant (Koc)

- Human health information: toxicity and exposure limits, maximum concentration in drinking water etc.

- Ecotoxicology: toxicity data for a range of fauna and flora, bioaccumulation

For a sustainable use of natural resources, especially of soils and ground water, more exact knowledge about physical, chemical and biological behavior of chemicals in the environment is needed, especially in view of possible accumulated effects through cross reactions between chemicals and their fate in the soil and ground water system. Little information is available about the economic benefits of controlling the use of chemicals in the environment, due to their medium to long term impacts. However, there is a need to inform politicians and decision makers about the risks of contaminants in the soil and ground water system with regard to the protection of basic human rights: clean food and clean water.

Therefore, the dissemination of our findings and conclusions from one year's literature review seems to bi important. We will publish our results in a form which can be understood by politics and decision making as well as by stakeholders and the broad public.

2 Aims and comparison with predetermined objectives

The **general goal** of this project was literature research on mobilization and immobilization processes of organic pollutants in the soil and ground water system to assess strategies for the prevention and the risk-based management. The state-of-the-art in this area is identified based on one year literature review. The results are given in the form of a report focusing on the main mechanisms and processes governing the transport and the fate of organic contaminants in soil and ground water. Moreover, detailed information about specific project tasks given in the separate research report of the individual partners. In these reports the influence of land use and climate change on the natural attenuation and mobilization processes is highlighted. Innovative strategies are elaborated on the basis of research results and methodological knowledge, thus contributing to the long-term risk-based management of organic soil and groundwater pollution. These results were discussed with end-users at the 2nd Workshop in Vienna.

On the one hand our literature research was specially focused on retention processes pollutants by different soil constituents, looking at the strength of binding forces and the long-term stability of such compounds. On the other hand, we looked at the pollutant mitigation based on biodegradation processes. Also, different case studies for current and emerging organic pollutants are presented in this report. The risks caused by mobility of non-bound or less-bound pollutants and the release of OM-colloids loaded with pollutants was defined on the basis of mobilization and leaching processes of organic pollutants. The spreading of pollutants caused by colloidal transport on long distances in the soil and groundwater system as indicated in the literature was described with special focus on the time scale and the risks caused by those fractions. The current knowledge of the soil binding processes allowed also for determining the limits of natural attenuation for mitigating risks as well as for describing the gaps in the current state-of-art of the attenuation processes.

3 Results

3.1 IfBk: Literature review

Main mechanisms, processes and factors governing the fate of organic contaminants in the soil system

- Strategies for innovative management -

3.1.1 Introduction

Soils play an important role in the regulation of contaminants in ecosystems. Soil constituents can attenuate potentially toxic concentrations of contaminants and accordingly diminish the risk of surface water and groundwater contamination. For instance, silicates, oxides and organic matter can adsorb organic pollutants, promoting their degradation to nontoxic forms, attenuating their movement through the soil, or preventing their uptake by plants and their introduction into the food chain. This so called “natural attenuation” relies on natural processes to immobilize, degrade and dissipate contaminants in soil and groundwater; these processes include physical, chemical and biological mediated reactions (e.g. aerobic/anaerobic biodegradation, dispersion, volatilization, oxidation, reduction, and adsorption) (Kao and Borden, 1997; Cozzarelli *et al.*, 2001; Bockelmann *et al.*, 2001). However, predicting the fate and behavior of organic contaminants is still difficult due to (i) a large range of components with different properties, (ii) a variety of complex dynamic physical, chemical and biological processes and (iii) spatial heterogeneity and transient conditions in the unsaturated soil zone.

In this literature study, the state-of-the-art knowledge on the main mechanisms, processes and factors governing the fate and behavior of organic contaminants in the soil system is reviewed. Special attention was directed to the use and improvement of the natural attenuation capability of soils as a cost effective and valuable tool in the management of soil contamination and prevention of groundwater pollution.

3.1.2. Organic Contaminants – Origin, pathways and related risks

Organic contaminants are mainly man-made and created in industrial processes, either intentionally or as by-products. The environmental release then poses an immediate threat to air, soil, surface water and groundwater quality through volatilization into the atmosphere, retention of the spilled chemical by the soil, runoff to surface waters and infiltration to groundwater. Some of them are known to disrupt normal function(s) of the endocrine systems in organisms and consequently cause adverse health effects in an intact organism, its progeny or (sub) populations (Gelbke *et al.*, 2004; Ying *et al.*, 2004).

Of high concern is that, the number of chemicals in our environment is rapidly growing and that until now, even a small number of these substances were subject of studies (Fig. 2). Consequently sufficient experimental data for detailed risk assessments is often missing (Wackett, 2004; Asano & Cotruvo, 2004).

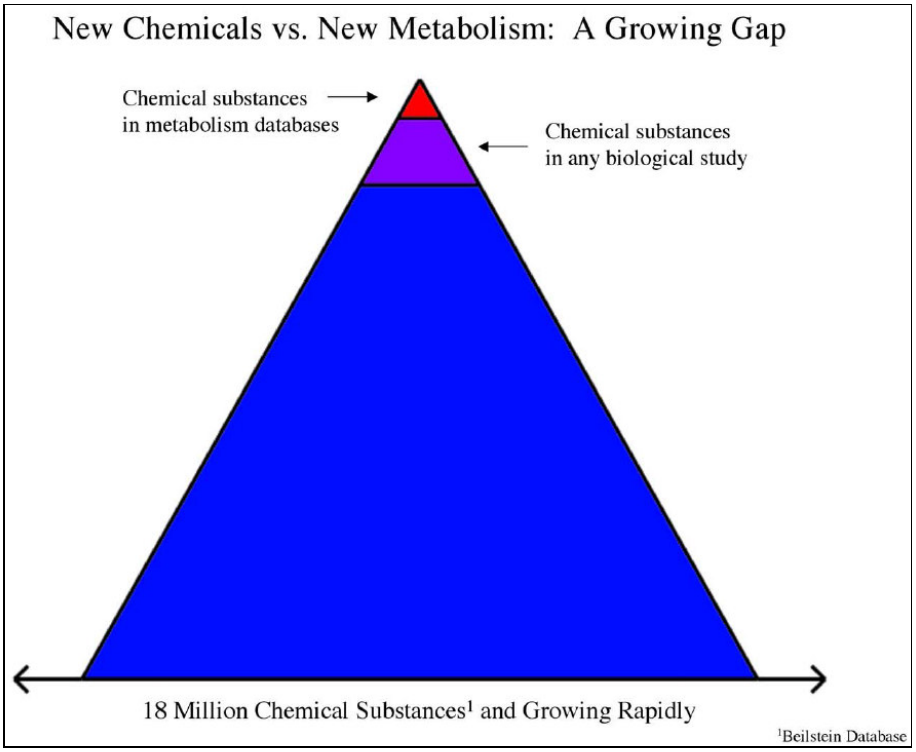


Fig. 2: The number of potential toxic and environmental harmful chemical substances is rapidly growing (Wackett, 2004).

Of concern are also contaminant metabolites and transformation products, which are in some instances more toxic and persistent than the parent molecule, and hence, might represent a greater risk (Megharaj *et al.*, 1999). Tests were mainly performed on single compounds, but recently there is evidence that organic contaminant mixtures might pose may be as yet unknown synergistic adverse effects (Carpenter *et al.*, 2002; Wade *et al.*, 2002; Ribo & Rodgers, 2006).

The analytical accessibility of complex substance mixtures and low concentrations is still difficult. The degradation products formed can comprise an extremely complex mixture of substances. For example, Lerch *et al.* (2003) reported that 28 different metabolites of trifluralin were formed in soils, and, because standards were available for only trifluralin and six of its metabolites, the other trifluralin products can only be identified using Tandem mass spectrometry (MS/MS). This points out that there are also gaps and limitations in analytics. Therefore, the significance to human health risk could remain unknown (Fig. 3). As a consequence, not all substances can be accurately described as contaminants or pollutants.

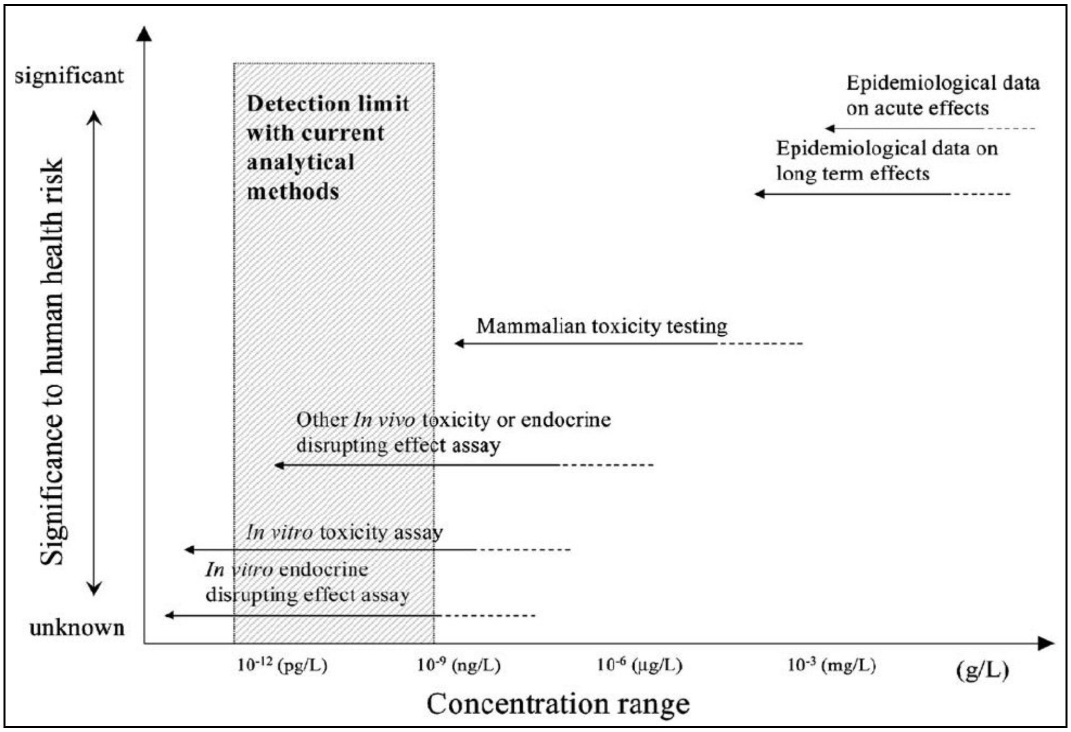


Fig. 3: Conceptual framework for various assays for trace organic compounds and their relative significance to human health risk (Asano & Cotruvo, 2004).

The analytical accessibility of the substances is a prerequisite for risk assessment. Accordingly, the development of high resolution techniques and suitable methods for laboratory and field analysis are of primary importance.

For further reading on contaminant monitoring and analyses

The most relevant analytical methods for determining pesticides and their transformation products in soils were reviewed from Andreu & Pico (2004). Recent advances in sampling and sample-preparation technologies for soil analysis and advantages and disadvantages of the various methodologies have been addressed in this study. In addition, O`Connor & Aga (2007) discussed in a review several strategies for sample preparation, extraction, clean-up and analysis of tetracyclines and their transformation products in soil, with the aim to facilitate future environmental fate studies, and to challenge analytical chemists to develop the necessary tools to allow a complete risk assessment of other pharmaceutical contaminants in the environment. screening techniques like biologically based assays (BBAs) may provide major advantages by estimating the total estrogenic effects of many e-EDCs in the environment and may potentially be adapted for field portable biologically directed sampling and analyses (Campbell *et al.*, 2006). In this review available BBAs used to measure estrogenic e-EDCs in the environmental samples and also present results relating to fate and transport of e-EDCs are summarized. Several of these issues were also covered by Ying *et al.* (2004) in a literature review performed within the frame of the ”Australian Water Conservation and Reuse Research Program” on trace organic constituents in recycled water in Australia. In this study many chemicals and naturally produced hormones contained in sewage have been detected at very low concentrations. Environmental and health considerations, awareness in risk management demands and research to fill current knowledge gaps were addressed in this study under the categories; sources, fate, receptors and risk assessment.

These hyperlinks guide you to the website of the (http://www.clw.csiro.au/awcrrp/) “Australian Water Conservation and Reuse Research Program”, where you can find several project reports and the literature review on Endocrine Disrupting (EDCs) including Pharmaceuticals and Personal Care Products from Ying *et al.* (2004).

3.1.3. Properties of organic contaminants and reactive soil constituents – the basis for the prediction of the fate of organic contaminants

Organic chemicals enter the unsaturated soil environment through various activities including accidental spills, leaking underground storage tanks, improper waste disposal and landfill leachate. When organic chemicals are released to the soil, they enter a three-dimensional heterogeneous environment composed of soil minerals, soil organic matter, soil water, soil vapors and biota. All these compartments vary in size form and composition. Thus, small scales and spatial heterogeneity of soil makes the estimations of physical and physicochemical conditions extremely challenging (Chenu & Stotzky 2002). The range of components is large and they interact with each other in complex ways (Wauchope *et al.*, 2002).
However, the fate and behavior of a specific organic chemical depends primarily on the three basic processes: (i) retention, (ii) degradation, and (iii) transport (Fig. 4). Both, the direction and rate of these processes are strictly dependent on the chemical nature of the contaminant and the physical, chemical, biological, and hydraulic properties of the soil. Accordingly, the fate of a contaminant can be predicted, with some accuracy, by knowing selected properties of both, the organic contaminants and the adsorbents (Arditsoglou & Voutsa, 2008) (see also chapter 3.3.6.3).

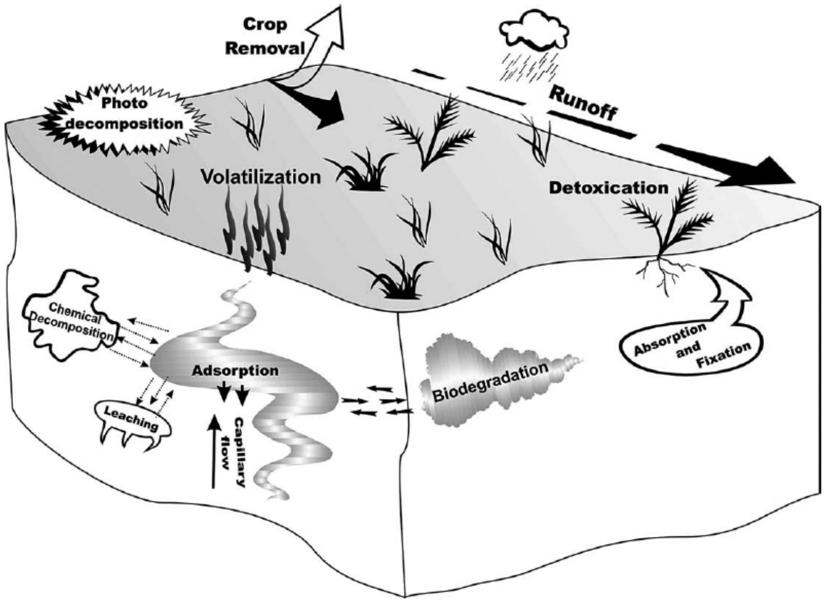


Fig. 4: Fate of organic contaminant residues in the soil (Andreu & Pico, 2004)

3.1.3.1 Significant properties of organic chemical substances

The physico-chemical properties of an organic chemical substance are dedicated by the structure of the molecule and the nature of the atoms present in the molecule. In the soil system, organic contaminants can occur in the solid, liquid and gas phase (see also chapters 4.2.1.2 and 4.1).

Volatility

The partition of a compound between water dissolved and air phases is described by the Henry's Law Constant. The higher the constant, the more likely a chemical is to volatilize than to remain in water. Organic chemicals that tend to vaporize and enter the atmosphere, under normal environmental conditions, are referred to as volatile organic compounds (VOCs), whereas semi-volatile organic compounds (SVOCs) evaporate slowly and incomplete when exposed to the atmosphere. Typical VOCs of different classes, the major processes determining their retention by soils, the main rules and mechanisms of VOC sorption, and the experimental methods of its measurement are reviewed in detail from Breus & Mishchenko (2006).

Hydrophobicity

Quite a few organic contaminants have also polar functional groups that enable the formation of hydrogen bonds. Thus, they are hydrophilic and water-soluble. However, most organic contaminants are non- or only weakly-polar and hydrophobic. These substances are unable to form hydrogen bonds, and so they are excluded from the aqueous phase and referred to as non-aqueous phase liquids (NAPLs). Their behavior depends strongly on the density. For example, light NAPLs will float on the capillary fringe, whereas dense NAPLs will sink until an impermeable barrier is reached.

Given similar structures of the organic molecules, compounds with higher molecular weights are commonly more hydrophobic and less volatile. Hydrophobic contaminants interact strongly with organic matter. The affinity for water and organic matter is usually described by the octanol-water partition coefficient (K_{OW}).

Environmental persistence and toxicity

Persistence in the environment is another important property. Persistent substances with recalcitrant chemical nature, low water solubility, high lipophilicity/ hydrophobicity and long degradation half-lives will be retained within the soil, and depending on the 'strength' of the association may persist for long periods of time (Semple *et al*., 2003). The potential of a substance to bioaccumulate and biomagnify in organisms is correlated to the lipophilicity and is expressed as the octanol-water partitioning coefficient Kow. Thus, hydrophobic organic compounds are often more toxic (Sikkema *et al.* 1995). The higher the persistence and the longer the time before a compound is broken down, the longer it may cause adverse effects.

Physico-chemical and toxicity data are accessible from a number of governmental agencies, universities, non-profit organizations, and commercial sources; many of these data are readily available online. This hyperlink (http://infotrek.er.usgs.gov/docs/nawqa_www/HBSL/reports/Phys-chem_and_tox_sources.pdfwill) guide you to a list of online sources for data on physical-chemical properties and toxicity for human and aquatic receptors. Helpful is also the "Handbook of Physical-Chemical Properties and Environmental Fate for Organic Chemicals, Second Edition" edited by Mackay *et al.* (2006)

Management - Registration, Evaluation, Authorisation and Restriction of Chemical substances

European Community Regulation on chemicals and their safe use deals with the **R**egistration, **E**valuation, **A**uthorisation and Restriction of **Ch**emical substances (REACH) and aims to improve the protection of human health and the environment through the better and earlier identification of the intrinsic properties of chemical substances. The European Chemicals Agency (ECHA) in Helsinki acts as the central point in the REACH system and provides a public database in which consumers and professionals can find hazard information. The regulation also calls for the progressive substitution of the most dangerous chemicals when suitable alternatives have been identified. For more information read: REACH in brief (http://ec.europa.eu/environment/chemicals/reach/pdf/2007_02_reach_in_brief.pdf).

Bit by bit, chemists in science and industry become aware of the importance to design environmentally benign chemicals. Such an interdisciplinary approach for the prospective design of environmentally benign substances and examples for new commodity chemicals that better fit the naturally existing catabolic potential are presented by Rieger *et al.* (2002).

3.1.3.2 Soil fractions and the nature and distribution of reactive soil surface sites

The particle size distribution of **soil minerals** determines the soil texture. In general the finest particles, clays and secondary oxides are by far the most important inorganic soil constituents for the retention of (i.e. ionic) organic contaminants in soils. Their small colloidal size and high specific surface area make them highly reactive and permit strong physical and chemical interactions with fluids and dissolved species.

An important feature of clay minerals is the presence of structural negative charges, which enables clay minerals to adsorb different kind of molecules, especially organic and inorganic cations (Rytwo *et al*., 2002;

Gürses *et al*., 2004; Lombardi *et al*., 2006). At very low pH, the edges of 2:1 and 1:1 clay minerals carry a positive charge, which makes them capable to interact with anionic compounds.

Fe, Al, Mn, Si and Ti oxides exhibit variable or pH-dependent surface charge, which is due to the amphoteric character of their surface hydroxyl groups. As a result, most oxides exhibit positive charge at low pH and negative charge at high pH. Oxides with high point of zero charge, e.g. for goethite and hematite between pH 6-9, are therefore important adsorbents for anionic organic and inorganic substances (Cornell & Schwertmann, 2003) (see chapter 3.3.6.4, 4.1. and 4.2.1.2).

Soil organic matter is composed of plant and animal debris and intermediates and end products of the decomposing debris (McRae, 1988). Organic matter is a complex material, which exhibits a dual character. The polar (negative or positive charged) functional groups are capable to interact with polar mainly cationic species, whereas non-polar (neutral charge) hydrophobic domains provide important sorption sites non-polar hydrophobic organic contaminants (Semple *et al.* 2003) (see chapter 3.1.2).

3.1.4 Immobilization of organic chemicals by soil constituents

The quantification and understanding of immobilization mechanisms are of fundamental significance for predicting the fate of organic contaminants in a specific soil. In addition, knowledge about these mechanisms is essential for the development of efficient methods for contaminated soil and aquifer remediation.

Sorption is generally the strongest interaction mechanism and can affect the fate of a contaminant in a number of ways. Apart from affecting mobility, and the potential for a contaminant to reach groundwater, sorption can affect the biodegradation and toxicity of a compound by influencing the bioavailability (Allard & Neilson, 1997; Guo, *et al*., 2000; Eggleton & Thomas, 2004; Arias-Estevez, 2008).

Generally, the soil organic carbon/water partition coefficient, Koc and the soil sorption/ partition coefficient Kd, are used to evaluate the sorption properties of a compound onto a sorbent surface at the water/solid interface. They are a measure of the strength of sorption and are thus directly related to the mobility and persistence (see also chapters 4.1 and 4.5).

Substances with low Koc or Kd values will show low adsorption and consequently high mobility and rapid transport into groundwater.

Koc and Kd values are used by environmental scientists and regulatory agencies worldwide in modeling, describing the environmental fate and behavior and for risk estimation. However, it is known, that these estimated parameters might be inexact or even not transferable from one site/soil to another. The major drawback of using Kd to predict leaching of contaminants is that it is highly dependent on soil characteristics. Koc is more independent from the soil type, but the determined values can be significantly affected by the solution parameters such as pH, ionic strength and presence of multivalent ions (Fig. 5). Thus, in a review article on the sorption of veterinary pharmaceuticals in soils, it has been addressed from Tolls (2001) that prediction of log Koc based on the hydrophobicity parameter log Kow is not successful.

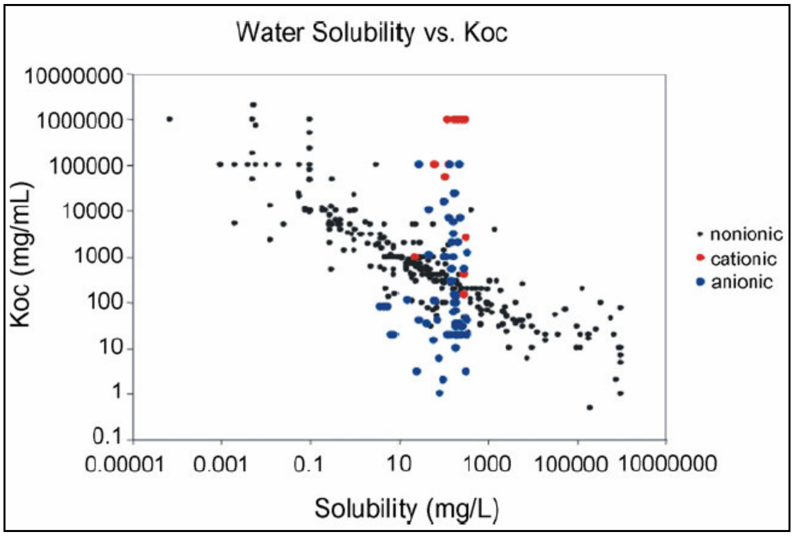


Fig. 5: Influence of water solubility on the Koc- value. Koc-values of polar substances (acidic or basic) are dependent on the dissociation constant of the substance and accordingly on the pH of the soil. These

substances do not fit the excellent regression observed for non-ionic pesticides between water solubilities and soil sorption coefficients (Arias-Estevez *et al.* 2008).

Wauchope *et al.* (2002) examined the theory, uses, measurement or estimation, limitations and reliability of these parameters and provided some "rules of thumb" for the use of these environmental parameters. Weber *et al.* (2003) correlated Kd values reported in literature with soil properties for an assortment of pesticides in an attempt to improve the accuracy of a Kd value for a specific chemical in a soil with known soil properties. They developed mathematical equations for 57 pesticides from regression equations for the related properties (organic matter content, clay content, and/or soil pH), depending on the chemical properties of the pesticide.

3.1.4.1. Sorption of organic contaminants

There are generally many intermolecular interactions involved in sorption, but the dominant processes depend on chemical-specific properties, such molecular size and configuration, and polarity or lipophilicity, as well as soil-specific properties, such as pH, organic matter content, clay content and amorphous iron oxide content.

For polar contaminants, surface interactions include ionic and/or covalent and hydrogen bonding. Anionic contaminants are only weakly sorbed by minerals with permanent charge, such as clays, because they are electrostatically repulsed from negatively charged surfaces. Thus, anionic contaminants have low soil sorption coefficients Kd (Wauchope *et al.*, 2002). They will be retained, to a limited extent, by positively charged sites of Fe-Al-oxyhydroxides and at low pH, on positively charged lateral edge sites of phyllosilicate minerals.
Cationic contaminants are strongly sorbed on permanent negatively charged clay mineral surfaces by cation exchange. They interact much more strongly with the solid phase of soils and sediments than anionic ones, since ionisable organic-matter moieties and clay mineral surfaces are generally neutral or negatively charged over the pH range found in the environment.

For non-polar contaminants, the non-polar hydrophobic domains of organic matter provides important sorption sites and binding through hydrophobic interactions (van der Waals forces) will dominate the contaminant sorption (Wauchope *et al.*, 2002; Semple *et al.* 2003). Sorption may be adsorption to the surfaces of soil organic matter or absorption into the organic matter, depending on the properties of the soil organic matter. The sorption of non-ionic substances has been broadly investigated and seems to depend on soil organic matter content (Gao *et al.*, 1998; Spark and Swift, 2002; Coquet, 2003). Beside this, it has been proved that the sorption depends on the molecular nature of soil organic matter (Ahmad *et al.*, 2006).
It has been shown that sorption of hydrophobic organic contaminants to soil organic matter may be controlled by the amount of aromatic carbon (Abelmann *et al.* 2005), aliphatic carbon (Simpson *et al.* 2003, Chen *et al.* 2007), or the polarity of the soil organic matter (Tanaka *et al.* 2005). The particle- or aggregate state of the organic matter includes portions with both fluid and rigid characters referred to as "rubbery" and "glassy", respectively (Xing & Pignatello 1997). Hydrophobic organic compounds may thus both adsorb onto surfaces and micropores of "glassy" and absorb into "rubbery" portions of soil organic matter, resulting in different sorption kinetics (Schwarzenbach *et al.* 2003, Pan *et al.* 2007). Besides, it has been suggested that soil organic matter may change its conformation between "rubbery" and "glassy" when, for example, pH changes (Feng *et al.* 2006). As a general rule, the higher the organic matter content of a soil, the greater the degree of adsorption of hydrophobic contaminants. However, Müller *et al.* (2007) showed that also mineral surfaces could significantly contribute to the retention of hydrophobic organic contaminants, especially in subsurface soil horizons and aquifer sediments with small amounts of organic matter. The link between structure and physico-chemical properties of geosorbents and sorption activity of hydrophobic organic pollutants upon interaction with solid matrices has been established recently (Ehlers & Loibner, 2006). The conclusions are from high importance for studies on risk assessment and remediation (see also chapter 3. 2.1).

3.1.4.2. Effect of soil solution composition - competitive sorption

The soil solution is a multifaceted aqueous soil solution, which contains a mixture of organic and inorganic solutes and the chemical reactivity of soils is affected by aqueous phase processes (e.g. hydrolysis, hydration, redox, dissolution / precipitation). Thus, the fate of an organic contaminant can be strongly influenced, depending on the nature and properties of the present solute species. As an example, the presence of harmless organic anions such as ones added by fertilizers and dissolved organic matter (DOM) can diminish the adsorption of anionic contaminants (from acids) due to competition for the same positive charged sorption sites. For example, Li *et al.* (2005) performed batch adsorption experiments and showed that the presence of DOM, extracted from two commercial organic fertilizers, reduced the sorption capacity for three organic chemicals (2,4-D, naphthalene and chlorpyrifos) with increasing DOM concentration in solution.

In contrast, the presence of multivalent cations such as Ca^{2+} might enhance the sorption of organic contaminants. For example, deJonge & Woolensen deJonge (1999) showed that sorption of glyphosate on a sandy loam bulk soil varied strongly in response to the solution composition, with higher sorption in presence of $CaCl_2$ (Fig. 6).

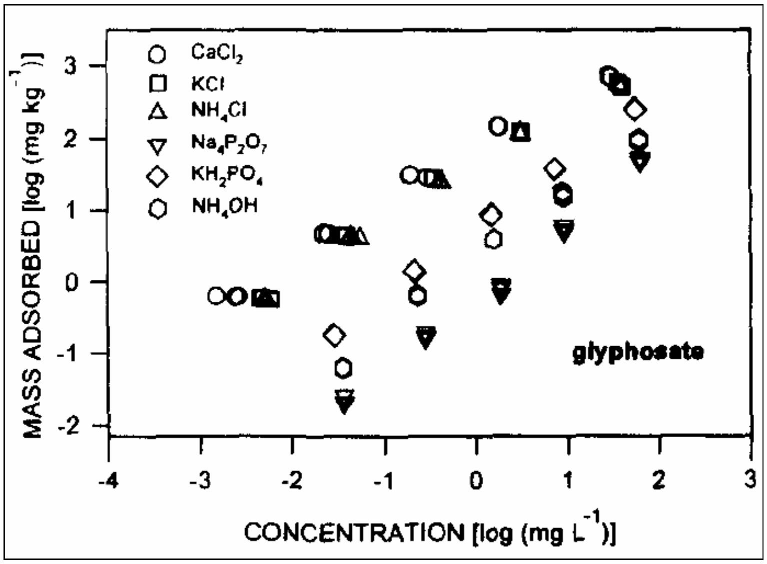


Fig. 6: Adsorption of glyphosate to a sandy loam bulk soil for the different salts at intermediate ionic strength (deJonge & Woolensen deJonge, 1999).

The higher adsorption is most likely due to the ability of multivalent cations to form bridges between negatively charged groups (Vermöhlen *et al.*, 2000) resulting for instance, in the formation of ternary complexes between contaminants and organic matter (MacKay and Canterbury, 2005).

In contrast, divalent cations have been observed to decrease the sorption of non-polar hydrophobic contaminants (HOC). Murphy *et al.* (1994), Jones and Tiller (1999) and Laegdsmand *et al.* (2004) found that the sorption HOC decreased with divalent cations. The presence of di- or polyvalent cations may also condensate the humic materials in the soil because of crosslinking (Murphy *et al.*, 1994; Pignatello, 1998; Lu & Pignatello, 2004) and blocking the diffusion paths to the interior glassy soil organic matter (SOM) (Laegdsmand *et al.*, 2004).

Minimal sorption of weakly and nonpolar compounds occurs on mineral surfaces in aqueous systems because of competition by water molecules (Wauchope *et al.*, 2002; Yong & Mulligan, 2004). It has been reviewed from Wauchope *et al.* (2002) that soils become extremely sorptive for both non-polar and polar species, when soils are very dry or water is replaced by a non-polar solvent. Then, competition by water for soil sorption sites is removed and clay mineral surfaces may become preferred sorption sites. On the other hand, low-polarity HOCs might be released when the soil is re-wetted.

In general, it can be concluded that the soil solution composition might dictate the potential for retention and ultimately the transport of contaminants to groundwater. Therefore, analyzing the soil solution can provide important information's on the dominant chemical, hydrological, biological, and geological processes occurring in soil. But, as addressed by McCharty and McKay (2004) sampling of soil and groundwater remains a critical challenge because traditionally applied sampling methods like drilling and pumping can often cause changes in chemical and physical solution properties.

3.1.4.3. Effect of pH on organic contaminant sorption

The pH is nearly the most important parameter in soils and its significance for the fate of organic contaminants has been highlighted in several studies (Wauchope *et al.*, 2002; Müller[a] *et al.*, 2007; Arias-Estevez *et al.*, 2008). Variations in pH affect the edge charge of clay minerals and the variable surface charge of Fe and Al oxides and ionisable organic matter moieties. Thus, for anionic contaminants bindings are expected to decrease with increasing pH so that desorption, mobility and transport is favored. In contrast, it has been addressed from Müller[a] *et al.* (2007) that an increase in soil pH may have a positive impact on the total number of available binding sites for weakly basic contaminants (Fig. 7).

Beside, sorption also depends on the chemical nature of the compound. Accordingly, it must be considered that changes in pH might affect the charge properties of the contaminants, which is due to dissociation and protonation of their functional groups (Wauchope *et al.*, 2002; Stephen *et al.*, 2005; MacKay & Canterbury, 2005). As reviewed from Wauchope *et al.* (2002) soil pH changes will have minor effects on the adsorption of non-ionic molecules, whereas sorption of substances with ionic equilibrium constants near the range of soil pH will be quite sensitive to the pH changes. For instance, Drillia *et al.* (2005) studied the sorption behavior and mobility of six pharmaceuticals (carbamazepine, propranolol, diclofenac sodium, clofibric acid, sulfamethoxazole and ofloxacin) in two soil types with different organic carbon and clay content, and in bacterial biomass (aerobic and anaerobic). They found that the adsorption of pharmaceuticals was also dependent on the dissociation degree of the compounds.

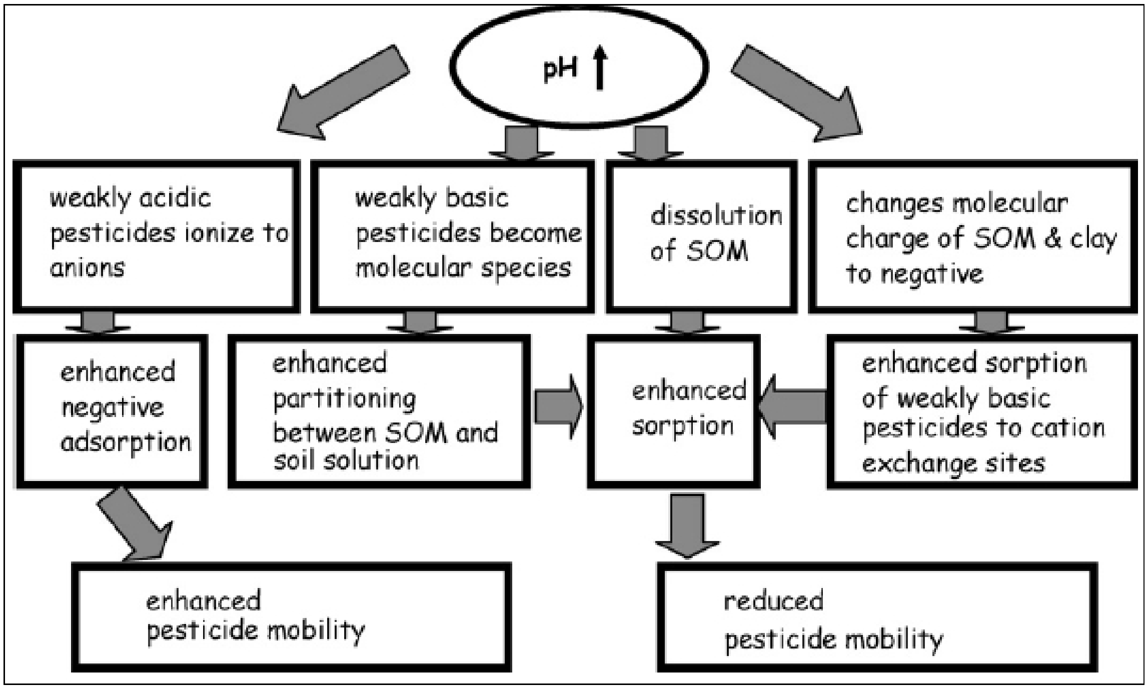


Fig. 7: Pesticide/ organic contaminant sorption and transport as affected by an increase in pH (Müller[a] *et al.* 2007).

The lowest sorption is expected, when increasing soil pH ionizes weakly acidic contaminants so that they become anions. Then, repulsion from the mainly negatively charged soil surfaces increases and sorption decreases. This effect will be amplified by a decrease of the pH dependent surface charge of the variable charge soil minerals.

3.1.4.4 Effect of DOM on contaminant sorption and retention

As addressed from Müller[a] *et al.* (2007), the presence or also addition of DOM can strongly affect organic contaminant sorption, degradation and transport because it can form complexes with organic molecules and/or can compete with organic molecules for sorption sites enhancing the contaminant mobility (Fig. 8). In contrast, the presence of DOM might also diminish the contaminant mobility due to co-adsorption of DOM–contaminant complexes onto the soil matrix. Nevertheless, partitioning of neutral contaminant species onto DOM is likely to enhance its apparent solubility and to reduce its sorption to soil solid components (Müller[a] *et al.*, 2007).

It was found that the potential impact of DOM on organic contaminant sorption depends on the following DOM characteristics: concentration, biodegradability and stability, size distribution, polarity and aromaticity and content of hydrophobic DOM fractions.

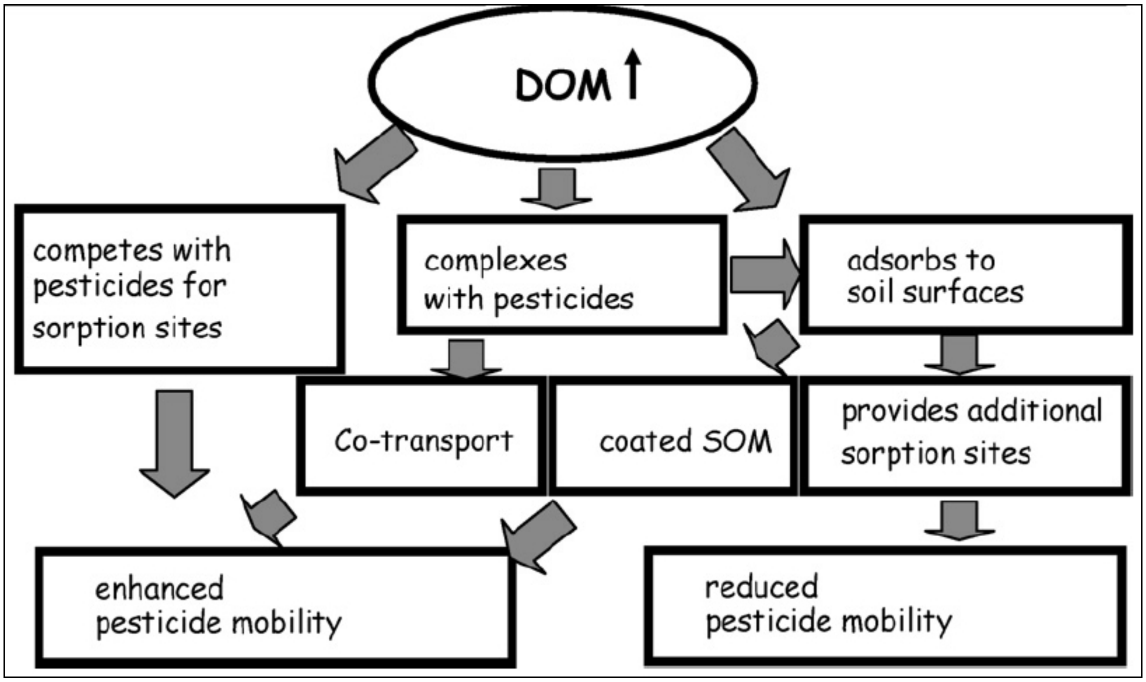


Fig. 8: Pesticide sorption and transport as affected by an increase in DOM (Müller[a] *et al.*, 2007).

3.1.4.5. Time dependent contaminant sorption

Sorption and desorption processes may differ in extent or time as reviewed by Doucette (2003). For example, Park *et al.* (2004) studied the effects of aging on mechanism-specific sorption and desorption of atrazine and they found that when normalized to soil organic matter content, the concentration of atrazine in desorbable sites was relatively constant, whereas that in non-desorbable site increased as a function of aging time in all soils. In general, long contact times will allow molecular diffusion of contaminants to the smallest pores of soil particles, which might result in strong sequestration of some organic chemicals and to the formation of strongly bound contaminant residues, as reviewed by Barraclough *et al.* (2005) and Barriuso & Benoit, (2006). Desorption of these sequestered contaminants is time consuming or even nonexistent and might affect the biodegradation rate (McLeod & Semple 2000). Thus, the future fate and behavior of these bound residues, as well as a possible release is not easily predictable. It has been recommended from Barraclough *et al.* (2005) that further investigations should be directed on the biological significance of such residues and their release.

3.1.4.6. Summarization of the main factors governing the sorption and retention in the soil

From the above sections, it becomes obvious that predicting the sorption/retention of an organic contaminant in the soil and groundwater system is not a simple issue. The range of components is large, the soil is heterogenic, the chemical conditions in the soil are highly transient and contaminant properties might be affected by chemical and biological processes. However, same generalizations can be made. The table below gives an overview of the main factors, which might either decrease or enhance the adsorption of a specific contaminant in the soil (Tab. 2).

Interactions of solutes and solids in natural soil and groundwater systems are mainly dependent on charge properties which, in turn, also depend on the pH-value and the kind and concentration of organic and inorganic cations and anions present in the soil solution.

Table 2: Contaminants, their main geosorbents in the soil and factors influencing the sorption

Contaminant/ metabolite properties	Main sorbent in the soil	Main factors influencing the sorption
<u>**Polar / hydrophilic**</u>		

Anionic	**Oxides** (lower sorption on edge sites of phyllosilicate minerals and ionisable organic matter moieties, depending on pH)	• **Oxide content**
		• **pH**: highest adsorption at low pH (related to AEC)
		• **solution composition:**
		  • competitive multivalent anions => decreased sorption
		  • multivalent cations => enhanced adsorption (cation bridging, ternary complexes)

Cationic	**Clay minerals** (lower sorption on oxides and organic matter)	• **clay content and mineralogy** (CEC) • organic matter and oxides could block adsorption sites • relatively strong sorption in nearly every soil
<u>**Apolar / hydrophobic**</u> **Non-ionic**	**Organic matter** (lower sorption on mineral surfaces)	• **organic matter content and composition** • **multivalent cations** => metal ion cross-linking, decreased sorption
<u>**Amphoteric**</u>		
Weakly acidic	**Oxides and organic matter**	• **very sensitive to pH** • **with increasing pH, compound becomes anionic and sorption decreases** • (same factors as for anionic compounds)
Weakly basic	**Clay minerals and organic matter**	• **very sensitive to pH** • **sorption increases with increasing pH** • (same factors as for cationic compounds)

3.1.4.7. Measurements to enhance the sorption and retention of organic contaminants

pH adjustment

Sorption properties of a molecule can be modified by pH adjustment. The pH in soil or water can be increased through addition of lime, calcium hydroxide, calcium carbonate, magnesium carbonate, etc. To lower the pH, sulphur compounds such as sulphuric acid can be used (Dupont *et al*., 1988). This may affect several other conditions in the soil system, e.g. it may affect the microorganisms, thereby influencing the degradation rate.

It is also noteworthy, that pH adjustment is not a long term solution because if the pH is changed again by e.g. natural soil acidification, contaminants will become mobile again.

Addition or incorporation of suitable adsorbents

For long term immobilization, not only pH, but also amendments that would bind the contaminants should be considered. This means, addition of those soil fractions or more generally adsorbents that have the greatest sorption capacity for a specific contaminant. For instance, Arias-Estevez *et al.* (2008) reviewed that organic amendments added to the soil is becoming a common practice. Increasing the organic matter content of a soil, would provide additional binding sites for non-ionic hydrophobic substances.

For the adsorption of anionic contaminants, higher oxide contents would be beneficial. The oxide content in the top soil can be increased by in situ oxidation of powdered Fe. Another measurement would probably be the utilization of red mud, a by-product of bauxite processing, which has already been used in agricultural situations (e.g. for use in acidic soils (because of its alkaline nature), as a substitute for agricultural limestone, as an amendment for acidic sand belts, as a treatment for iron deficient soils, in sandy soils to increase phosphorous retention etc.). More information on the various applications of red mud can be found on http://www.redmud.org. Novel applications of red mud as a coagulant, adsorbent and catalyst for environmentally benign processes were also described in a review article from Wang *et al.* (2008). Incorporation of organic matter, clay and oxides might be also positive for the physical conditions such as aggregate stability and water holding capacity of a soil (see also chapter 4.4.2).

3.1.5. Mobility and transport of organic contaminants in the soil

It is well known that organic contaminants and/or their metabolites can eventually pollute the groundwater after moving through the unsaturated soil zone (see also chapters 3.3.4 and 3.3.6.10). In general, the downward displacement of contaminants is strongly correlated with the sorption/ retention by the soil constituents (Müller $_a$ *et al.* 2007; Reichenberger *et al.* 2007; Arias-Estevez, 2008). Compounds that are strongly adsorbed onto soil are not likely to leach, regardless of their solubility. In contrast compounds that are weakly sorbed will leach in varying degrees depending on their solubility. As water is the carrier, organic contaminants that dissolve readily in water have greater potential to move downward through the soil, possibly reaching the groundwater. The leaching risk will be lower for volatile compounds simply because, it will be lost to the atmosphere and the less that remains available for leaching (Reichenberger *et al.* 2007). The probability of an organic contaminant to volatilize is a function of both its vapor pressure and its solubility and expressed by Henry's Law Constant. Contaminants with low Henry's Law Constant exhibit a greater leaching potential.

Nevertheless, the rate and magnitude of rapid transport is generally influenced by multiple factors, including not only contaminant properties, but also soil properties (e.g. organic matter, clay content, Fe-oxides, etc.). Additionally, soil structure, hydrological processes and management might have an important influence on contaminant transport (Malone *et al*., 2003; Montoya *et al*., 2006; Green *et al*., 2003; Li *et al*., 2005; Müller^a *et al.* 2007).

Highest leaching/ risk is generally expected for highly soluble, non-volatile and weakly sorbing contaminants (e.g. anionic substances) and in soils consisting of weakly sorbing constituents (e.g. low organic matter, clay and oxide content), climates with high precipitation and low temperatures (which leads to high groundwater recharge), and in soils with high permeability.

3.1.5.1. Runoff, Erosion and Volatilization

Increased runoff and volatilization are related to a contaminant loss at a specific site. Thus, contaminants, which are subject to runoff, erosion and volatilisation, do not contribute to leaching any more (Reichenberger *et al*., 2007; Breus & Mishchenko, 2006). However, runoff, erosion and volatilization can not be seen as real attenuation processes because contaminants became just displaced to another site. In consequence, surface runoff, erosion and volatilization are simultaneously also sources of organic contaminants.

One measurement to reduce pesticide inputs into surface waters via runoff and erosion is the use of vegetated buffer strips along field edges and water bodies (see also chapters 3.3.6.11 and 4.2.1.2) (Fig. 9).

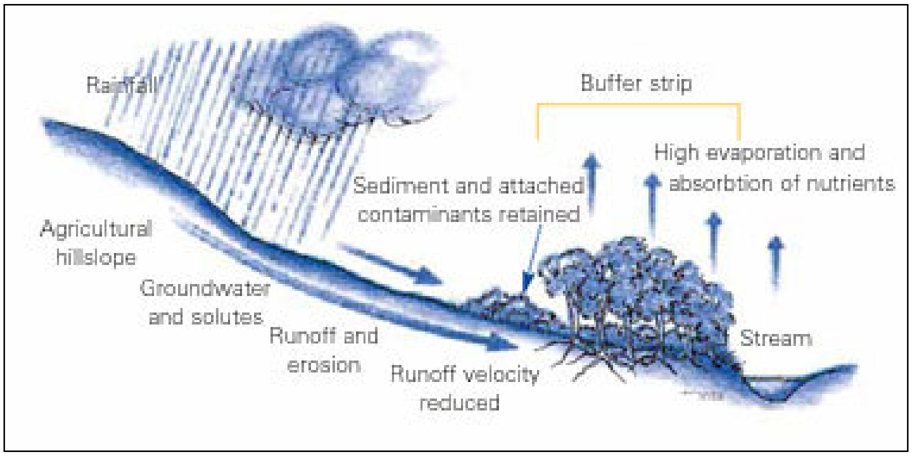


Fig. 9: Schematic illustration on the function and placement of buffer strips in landscapes (Land & Water, Australia).

The effectiveness of buffer strips in removing pollutants was subject of many studies. The results point out that buffer strips could be an efficient and economical way to reduce agricultural no point source pollution (Borin *et al.*,2005; Dorioz *et al.*, 2006; Duchemin & Hogue, 2008) consequently representing a potential management strategy for agricultural pesticides (Reichenberger *et al.*, 2007). Environmental benefits of buffers, the economic issues related to buffer adoption, the importance of the aesthetic quality and design of buffers, and areas in which future research is necessary to improve buffer functionality and adoption were reviewed by Taylor Lovell & Sullivan (2005).

3.1.5.2. Preferential flow and colloid associated contaminant transport

There are also exceptions to the previously posted rules. Precisely because, it was observed that even strongly sorbing organic contaminants may be transported rapidly to groundwater by bypassing the soil zone. Hypotheses proposed to explain such a rapid transport include preferential flow, co-transport with colloidal particles, and also a combination of these both processes (Zehe & Flühler, 2001; MacCarthy & MacKay, 2004; DeNovio *et al.*, 2004; Kanti-Sen & Khilar, 2006.

This allows a much faster transport of a range of contaminants and shortens the residence time of a contaminant in the topsoil, where sorption is usually stronger and degradation is faster than in the subsoil thereby reducing the chances for biodegradation and transformation. This implies significant consequences for ground-water quality, drinking water supply and human health.

The problems with occurring of preferential flow pathways and colloid associated transport of contaminants are broadly addressed in literature. For instance, a state-of-the-art review on preferential flow was authored by Jarvis & Dubus (2006) and extensive scientific papers and reviews dealing with uncertainties in flow and transport in the vadose zone and subsurface colloids and colloid-associated contaminant transport can be found in a special section of the `Vadose Zone Journal` (http://vzj.scijournals.org/content/vol3/issue2/) and in a review article from Kanti-Sen & Khilar (2006).

The preferential flow phenomenon generally refers to the uneven and often rapid movement of water and solutes along certain pathways, while bypassing a fraction of the porous matrix. Mobile colloids in soils and groundwater aquifers have received considerable attention due to their ability to enhance the transport of various contaminants. Contaminants that are sparingly soluble in water and have a strong tendency to bind to the solid phase and form stable complexes hence they were assumed to be retarded in the soil. Nevertheless, field observations have revealed that several contaminants, such as strongly sorbing pesticides, can move much deeper and faster than would be supposed from traditional transport models based on column or batch experimental data (Williams *et al.*, 2000; McCarthy & McKay, 2004). Spatial variability or transport through zones of fast flow (preferential flow phenomena) has been assumed to be responsible for some of the inconsistencies between predictions and current leaching of contaminants.

Today, it is generally accepted that the presence of macropores (cracks, soil fauna channels, and root holes), soil hydrophobicity and soil profile heterogeneity may cause rapid or preferential non-equilibrium transport in the unsaturated soil zone. Once believed to occur exclusively in structured soils, preferential flow is now recognized as prevalent under a wide range of conditions, in permeable soils with unstable poor structure as well as those containing cracks and crevices.

The conditions under which preferential flow occurs and the factors that lead to mobilization or deposition of colloids have been broadly studied. The results reveal that the rapid transport of contaminants is strictly depended on the interaction of many factors such as soil texture, soil structure, permeability of subsoil, soil hydrophobicity, temperature, rainfall distribution, agricultural management.

Effect of Agricultural Management on Soil Hydraulic Properties

Especially, tillage practice is often reported to affect the mobility and transport of contaminants due to changes in the hydraulic properties. But the effects of different tillage practices on the quantity of hydraulically active macropores and soil conductivity, is uncertain (Malone *et al.*, 2003 and Green *et al.*, 2003). In addition, the effects of soil texture and tillage system on atrazine transport through intact soil columns have also been evaluated by Montoya *et al.* (2006) and they concluded that most tillage practices seem to have only pronounced short-term effects on soil hydraulic properties and that intrinsic soil properties are more relevant for atrazine transport than those associated with tillage practices.

Uncertainties in predicting preferential flow

From literature, it becomes quickly clear that transport pathways and mechanisms in the soil are very complex due to the chemical and physical heterogeneity of soils and extremely transient chemical conditions (e.g. due to introduction of low ionic-strength rainwater). The understanding of the physics of preferential flows is good, but linking such flows to observable soil-features is insufficient and for up- scaling and taking pore-scale understanding to heterogeneous & biologically active soils more research will be needed.

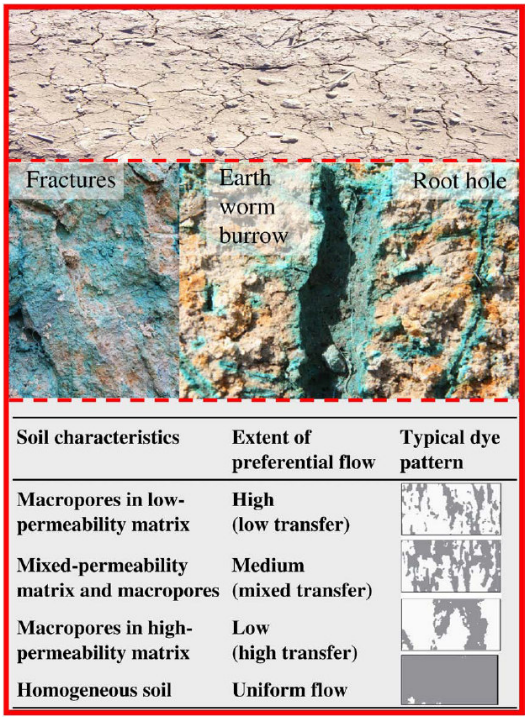
Accordingly, based on the current state of knowledge, it seems barely possible to delimitate the occurrence of preferential flow to specific soil types.

3.1.5.3. Summarization of the main factors controlling the contaminant leaching

As addressed before, the leaching potential is strongly correlated with the sorption properties of the contaminant and with the sorption ability of the soil. The main factors that govern the sorption and retention of organic contaminants were already compiled in Tab. 2.
Additionally, of great importance is also the contribution of preferential flow and the transported amount of colloid-associated contaminants. The knowledge of these parameters is also the prerequisite for the design of mobilization and immobilization strategies of colloids in certain soil systems.

Main factors controlling the occurrence of preferential flow pathways

However, the main factors controlling the occurrence of preferential flow pathways are probably: soil texture, structure and permeability as shown in Figure 10. In addition, water repellency or poor wettability of the soil surface and climate parameters such as seasonal temperature variations and rainfall distribution, are also expected to have a strong influence. Studies also indicate that the predominant preferential flow paths might be stable for decades, which might be of high importance for modeling flow patterns for solute transport (Hagedorn & Bunt, 2002).



Soil characteristics	Extent of preferential flow	Typical dye pattern
Macropores in low-permeability matrix	High (low transfer)	
Mixed-permeability matrix and macropores	Medium (mixed transfer)	
Macropores in high-permeability matrix	Low (high transfer)	
Homogeneous soil	Uniform flow	

Fig.10. Fractures and microtopography are triggers for preferential infiltration (top). Diverse structure/matrix interfaces stained by dye tracer visualize different preferential transport paths; these interfaces may affect lateral diffusion, sorption and degradation (middle). Soil matrix and macropore characteristics and resulting transport patterns; current patterns also depend on the characteristics of rainfall and of overlaying soil horizons (bottom) (Köhne *et al.*, 2008).

Main factors controlling the dispersion and mobilization of colloids

The interaction and behavior of surfaces or colloids is of quantitative significance in understanding the transport and fate of compounds and microorganisms in environmental systems. It is known that dispersion, mobilization and transport of colloids in natural, structured soils depends generally on complex interactions among soil characteristics controlling the inherent dispersibility of colloids, and on dynamic properties determining the prevailing conditions for colloid mobilization and transport. The mobilization and/ or deposition processes are generally dependent on physical and chemical parameters. For instance, Torkzaban *et al.* (2007) reviewed that the colloid deposition is highly sensitive to the physical (grain size, water content, and flow rate) and chemical (solution ionic strength and pH) properties of a system due to the interrelation of these parameters on colloid straining.

Physical parameters

Colloid migration is generally strongly dependent on colloid size and physical heterogeneity (Bradford *et al.*, 2004). The main physical processes affecting colloid movement in unsaturated porous media are shown in Fig. 11 and were described in detail by (DeNovio *et al.*, 2004). The experimental and modeling results from Torkzaban *et al.* (2007) suggest that the straining of colloids in low velocity regions of porous media such as grain junctions is the primary mechanism of colloid retention under both saturated and unsaturated conditions. The extent of stagnant regions of flow within the pore structure was found to be enhanced with decreasing water content, leading also to a greater amount of retention.

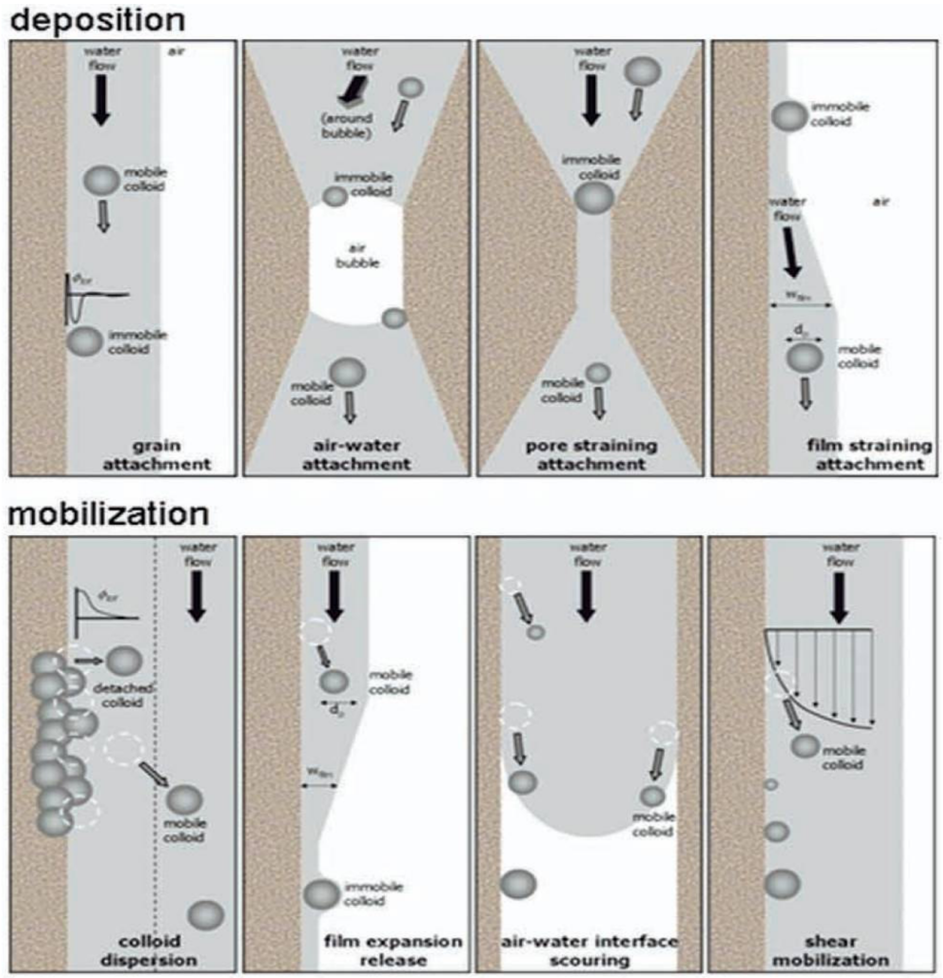


Fig. 11: Processes affecting colloid movement in unsaturated porous media. Colloid deposition mechanisms include attachment to grains by physicochemical filtration, attachment to immobile air–water interfaces (water flow is around bubble trapped in a pore), attachment by straining in water-saturated pores, and entrapment in thinning water films during draining. Colloid mobilization mechanisms include colloid dispersion by chemical perturbation, expansion of water films during imbibition, air–water interface scouring during imbibition and drainage, and shear mobilization (DeNovio *et al.*, 2004).

It has been reviewed by Totsche *et al.* (2006) that the release and transport of PAHs at contaminated sites is affected by three processes, i.e., (i) first-flush export, (ii) detachment of particle-associated PAHs due to hydraulic mobilization and (ii) the rate limited release of particles and particle-associated PAHs.

Crist *et al.* (2005) studied the transport, retention, and release mechanisms of hydrophobic and hydrophilic polystyrene latex microsphere colloids in slab chambers, filled with either regular (hydrophilic) or weakly water-repellent sand. Their results showed a greater retention of the hydrophobic colloids, which was attributed to strongly attractive hydrophobic interaction forces between colloids and subsequent filtering of colloidal aggregates in the narrow passages between grains. They concluded that once filtered, these aggregates then serve as preferred sites for attachment of other hydrophobic colloids. The hydrophilic colloids were retained primarily in a thin film of water at the edge of the menisci, the air– water–solid interface (Fig. 12). Sorption at the air–water interface was not observed and appeared unimportant to the retention of colloids.

Nevertheless, Chen & Flury (2005) concluded from their experiments that repulsive interactions exerted by the liquid–gas interface most likely leads to sediment attachment and higher colloid retention. Chen *et al.* (2007) explained this, with repulsive electrostatic interactions between the colloids and the liquid–gas interface, which aided colloids to overcome the repulsive electrostatic interaction barrier with the sediments, initiating the attractive Lifshitz–van der Waals interactions between colloids and the sediment and leading the colloids to attach to the sediments. In their study, the increase of the repulsive electrostatic interactions was greatly pronounced for colloids with greater surface charge densities and for colloids with greater surface charge densities a greater retention near the liquid–gas–solid interface as compared to colloids with less surface charge densities, was observed.

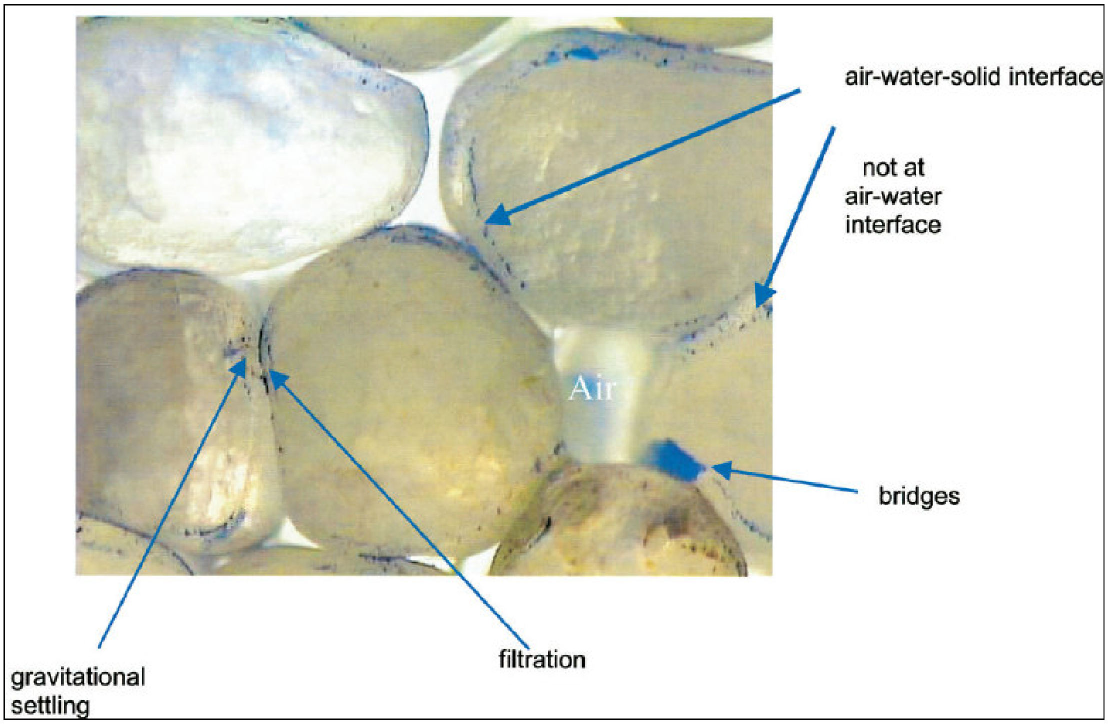


Fig.12. Various retention mechanisms of hydrophilic colloids: gravitational settling, filtration, colloids collection in bridges, and colloid retention at the air–water–solid interface (Crist *et al.*, 2005).

Chemical parameters

Next to these mainly physical aspects, variations of the chemical soil parameters have to be considered. Changes or variations of chemical parameters might have a strong influence on the charge properties of soil colloids and consequently on the dispersion. Derjaguin-Landau-Verwey-Overbeek (DLVO) model of colloid stability has described these interactions. This model finds its basis in a force (energy) balance that comprises attractive van der Waals and repulsive electrostatic interactions. According to the DLVO theory, the relationship between the surface charge and the state of dispersion is, the higher the surface charge, the higher the electrostatic repulsion between particles and the more dispersed the particles. But as reviewed by Grasso *et al.* (2002) the DLVO model has been found unable to fully describe biotic and abiotic colloidal behavior in aqueous media. In this article many of the interactions that play a role in environmental systems and are not commonly subsumed by the traditional DLVO model: e.g., hydrogen bonding and the hydrophobic effect, hydration pressure, non-charge transfer Lewis acid base interactions, and steric interactions, have been reviewed. In addition, Pochard *et al.* (2003) showed that the state of dispersion is not always correlated to the magnitude of the surface charge, but seems to depend on the surface density, and they found that even monovalent species present at the interface of mineral particles are deeply involved in the dispersion process.

However, there are a variety of uncertainties in fully describing the stability of colloidal suspensions, but it has been reviewed by Kanti-Sen & Khilar (2006) that the major factors inducing mobilization and transport of colloids are changes in solution ionic strength and pH. The release of particles in most soils is favored by high pH, high Na^+ saturation and low ionic strength. In addition, Elimelech and Ryan (2002) reviewed that addition of anions, surfactants and reductants often results in mobilization.

Field experiments have also shown that agricultural management practices like slurry application and plowing might increase the risk of particle facilitated and dissolved leaching (Schelde *et al.*, 2006). However, the decisive soil parameters for colloid transportability are listed in Tab. 3.

Table 3: Summarization of the main soil parameters and their consequences for the mobility and potential transport of colloids.

	Colloid Transportability
Soil Parameters	**Low High**
Preferential flow pathways	◢
Macropores	◢
Roots	◢
Colloid dispersibility	◢
Colloid size	◣
Moisture content	◢
Soil solution ionic strenth	◣
Flow velocity / rate	◢
Clay content	◣
Oxide / hydroxide content	◣

For further reading on transport mechanisms and processes in the soil system
Water flow in the soil and subsurface, non-equilibrium transport in preferential flow domains and various approaches for measuring, interpretation, modeling, and up-scaling issues were also covered in several review articles (Berkowitz, 2002; Simunek *et al.*, 2003; Köhne [a] *et al.*, 2008; Köhne [b] *et al.* 2008; Coppola & Kutílek, 2008).

3.1.5.4. Measurements to reduce contaminant leaching and groundwater contamination

Prevention of preferential flow and water repellency

Measurements to reduce or even eliminate preferential flow phenomena are relatively rare. In general, soil structure and climatic parameters cannot be influenced easily, but the wettability of the soil can be improved by various techniques and numerous management options for water repellent soils exist. Such management strategies and measurements for water repellency and risks associated with pesticide leaching due to preferential flow are described in detail in a review article from Blackwell (2000). The promising measurements for a sustainable soil management would include (i) reduction of soil surface drying, (ii) masking and degradation, and (iii) reduction of surface tension (see also chapters 4.2.1.1., 4.2.2, 4.3.1, 4.4 and 4.4.3).

Reduction of soil surface drying
Zero till methods can reduce soil drying by accumulation of crop residues to minimize soil drying and the development of water repellency and may employ dead root systems from previous crops and pastures to assist redistribution of water during infiltration.

Claying
Claying initially employs soil particles to cover the hydrophobic surfaces, and may encourage degradation of hydrophobic material by improved microbiological activity. Roper (1998) showed that relatively small amounts of clay and lime added to water repellent soil can encourage microbial degradation of hydrophobic material, presumably also organic contaminants.

Reduction of surface tension
By the employment of harmless (bio-)surfactants it is possible to reduce the surface tension and to enhance soil wetting *(Fig. 13).*

Fig. 13: In an experiment on a golf course (sandy soil) it was shown that high pressure injection of surfactants is a capable method to improve the wettability of the soil and to prevent the development of water repellence which influences infiltration behavior, and leads to irregular wetting and preferential flow. Another beneficial effect is that by use of surfactants, less irrigation water is needed to keep the soil water content above its critical value Dekker *et al.* (2004; 2006).

Reducing colloid dispersebility

Torkzaban *et al.* (2007) noted, that higher ionic strength contributes to the retention, because the number of colloids that are held in the secondary energy minimum increases with ionic strength. Thus, a lower displacement of high–ionic strength soil water with low–ionic strength rainwater may contribute to the inherently lower dispersibility in controlling colloid mobilization (Kjaergaard *et al.*, 2004).
In general it would be possible to increase the ionic strength can be increased by liming or gypsum amendments, but this is rather a preliminary measurement than a permanent solution. Permanent immobilization seems difficult. However, amendments of positively charged oxides as a treatment for iron deficient soil, might improve the aggregation and retention of the predominantly negatively charged colloids. As the addition of anions, surfactants and reductants might result in mobilization, this should be avoided (Elimelech and Ryan, 2002).

Measurements related to agricultural practices

It has been reviewed from Reichenberger *et al.* (2007) that also pesticide applicators can minimize leaching, by relatively simple measurements, which are often addressed in regionally specific recommendations and restrictions. These might include e.g. (1) usage of pesticides only when, and only in amounts required, (2) avoidance of irrigation directly after pesticide applications, (3) application of pesticides specifically to the target site, avoiding wells and surface water such as ponds and streams, (4) spray-application of pesticides only under calm, no-wind conditions, (5) safety pesticide storage and accurate disposal of pesticides, leftover pesticides, tank mixes, etc., etc.
Most farmers would generally choose the pesticide based on: (1) their purpose of use, (2) the product promotion, and (3) the price of the product. If the pesticide or the soil is susceptibility to leaching, is probably not in the main interest of the farmer. Thus, it is of high importance to police pesticide marketing, usage and to elucidate risks, best management practices etc.

Within the frame of the **FOOTPRINT-**project tools for pesticide risk assessment and management in Europe are created, which are intended to be used by 3 communities of end-users having different requirements with regard to pesticides: (1) Farmers and extension advisers at the Farm Scale, (2) Water managers and those in charge of implementing the WFD at the Catchments and Regional Scales and (3) EU and member states policy- and decision-makers, and pesticide registration authorities at the National and EU Scales. More information can be found on the FOOTPRINT website (http://www.eu-footprint.org/), which contains also several review articles dealing with e.g. preferential flow, formation of bound residues, mitigation strategies to reduce pesticide leaching etc.

3.1.6. Degradation and contaminated site remediation

Degradation is fundamental for attenuating organic contaminants in soil. The environmental persistence is largely controlled by the degradation rate, which is governed by both abiotic and biotic factors. It can follow complex pathways involving a variety of interactions among microorganisms, soil constituents, and the contaminant. Thus, degradation rates depend on many microbiological, physical and chemical properties of the soil, as well as the properties of the contaminant (see also chapters 3.3.2 and 4.4).

The field dissipation half-life is an empirical estimate of the length of time in which half of the original amount of the contaminant will disappear. This estimate takes into account physical, chemical, and biological degradation, plant uptake, and for highly volatile pesticides, volatilization. The longer the half-life, the greater the length of time the pesticide remains in the soil and, hence, the longer the opportunity to leach. The Half-life is difficult to predict because it varies widely for each compound and is highly dependent on the chemical, physical, and biological properties of the soil. Thus, estimated half-lifes cannot be accurately transferred from on soil to another.

It is very clear that ultimate degradability is a desirable characteristic for a contaminant in order to avoid pollution. However, it must also be recognized that partial biodegradation of a compound may result in the production of recalcitrant, more toxic and persistent intermediates, which represent a greater risk to the environment than the parent molecules (Sikkema *et al.*, 1995; Megharaj *et al.*, 1999; Arias-Estevez *et al.*, 2008).

3.1.6.1. Chemical degradation

A number of chemical processes such as hydrolysis, oxidation–reduction, substitution, elimination, dehalogenation and photolysis are responsible for organic contaminant degradation (Müller $_a$ *et al.*, 2007). It has been reviewed from Warren *et al.* (2003) that the two most important types of chemical degradation reactions are hydrolysis, usually either acid or base-catalyzed and oxidation and reduction reactions.

Hydrolysis is the reaction of a chemical with water. Hydrolysis of organic contaminants occurs in the root zone of soils and at slower rates also in groundwater. According to Müller $_a$ *et al.* (2007), factors that influence chemical hydrolysis include organic matter content and clay content with large surface area for enhancing hydrolytic conversion and soil pH, which greatly impacts on the hydrolytic process of organic contaminant dissipation. Hydrolytic degradation of organic contaminants increases with increasing temperature (Ayala-Luis *et al.*, 2006) and can be enhanced by supporting specialized microbial enzymes (Vasileva-Tonkova & Galabova, 2003). Hydrolysis can be a significant degradation pathway for compounds containing ester, ether or amide functional groups (for example s-triazine and carbamate pesticides) and for mono-substituted haloalkanes (Warren *et al.*, 2003).

Oxidation-Reduction reactions can occur in exchanges between organic contaminants and soil fractions under abiotic and biotic conditions. It is often difficult to distinguish between redox reactions that occur abiotically and those that occur under biotic conditions since direct involvement of any microbes cannot be readily ruled out. The major oxidants present in the environment are O_2, and Fe^{III} and $Mn^{III, IV}$ oxides. Results from Tobler *et al.* (2007) suggest that in anoxic soils and sediments containing amorphous and crystalline iron phases simultaneously, coupling of microbial oxidation and abiotic reduction of organic compounds may allow for concurrent natural attenuation of different contaminant classes. In general, the number of organic contaminants that can be oxidized or reduced under abiotic conditions is considerably smaller than those under biotic conditions (Yong & Mulligan, 2004).

Photolysis is a process in which breakdown of organic contaminants in aqueous solution is caused by exposure to sunlight. Both clay minerals and humic substances are reported to produce oxygen-reactive species (singlet and atomic oxygen, and hydroxyl radicals) when exposed to sunlight and contribute to enhanced photodegradation (Warren *et al.*, 2003; Müller ^{a} *et al.*, 2007).

Due to the small number of contaminants that will degrade directly following absorption of natural light (e.g. highly conjugated species such as polyenes, nitroaromatics etc.), direct photolysis is not generally a significant degradation pathway (Warren *et al.*, 2003). Nevertheless, for wastewater treatment, nanoscale photocatalysts have attracted much attention due to their high surface area to volume ratios and some of them (e.g. ZnO-nano) were successfully utilized for total cleanup of contaminated water (Hariharan, 2006). (see also chapter 3.3.6.11)

Tarr and Dekker (2003) edited a book with the title "Chemical degradation Methods for Wastes and Pollutants - Environmental and Industrial Applications", which offers an in-depth explanation of the degradation process, mechanisms, and control factors affecting each method, as well as issues crucial to the application of these approaches in real-world treatment sites.

3.1.6.2. Biological Degradation

Chemical degradation may generally result in a change in the property of a material and, although this will rarely cause complete breakdown, it may facilitate biodegradation. In general, the major degradation form in the soil is through oxidation and other reactions mediated by microorganisms (Fig.14).

According to Müller [a] *et al.* (2007) three main types of microbial transformation can be distinguished (see also chapters 3.3.3 and 4.1):

(1) Microbial metabolism: in which little or no degradation occurs on immediate exposure to the contaminant, but after a lag phase microbes adapt to use the added chemical as a source of carbon and energy for their growth.

(2) Co-metabolism: in which decomposition starts as soon as the contaminant reach the soil, mainly due to catalysis by extracellular enzymes already present in the microbial population. This is the most common form of degradation and in this process the contaminants do not serve as a direct source of energy but are transformed by metabolic reactions,

(3) Bioaccumulation: in which the compound is incorporated into the tissues of the organism itself by active or passive uptake processes (but not used for growth)

Metabolism and co-metabolism are the most important types of transformation. Metabolic or co-metabolic redox, hydrolysis and other reactions are usually faster than abiotic reactions for most types of compound, since microorganisms utilize enzymes as biological catalysts to increase reaction rates.

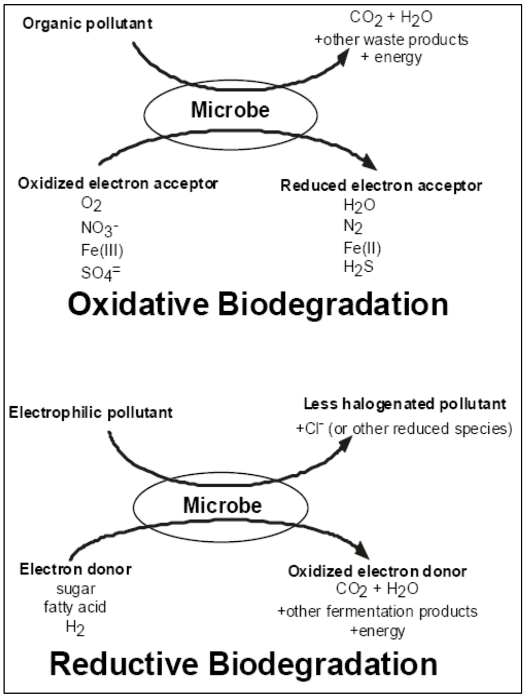


Fig. 14: General schemes to biodegrade organic pollutants.
In oxidative attacks (upper) pollutants are oxidized by external electron acceptors such as oxygen or sulfate. In reductive attacks (lower), electrophilic halogen or nitro groups on the pollutant are reduced by microbes consuming sugars, fatty acids, or hydrogen. The halo- or nitro- group on the pollutant serves as the external electron acceptor (Rockne & Reddy, 2003).

The microbial activity and degradation is strongly influenced by size and species composition of the microbial population, the chemical nature of the contaminant itself, temperature, soil water content, organic carbon content, soil pH, nutrient availability, and other environmental conditions. The presence of contaminants can enhance or reduce microbial activity depending on their bio-toxicity. For example, antibiotics can significantly reduce numbers of soil bacteria, resulting in dose related shifts in the fungal:bacterial ratio (Thiele-Bruhn & Beck, 2005). Thus, degradation rates are known to vary from one soil to another and even within a specific soil. Some of the major aspects and interdependencies that have to be considered are:

Distribution of microbes

The natural distribution of microbes in the soil has important implications for managing contaminants. The microorganisms that exist in the soil and which are involved in the biological degradation include all types from the five major groups; bacteria, actinomycetes, fungi, algae and protozoa (Alexander, 1977; Yong & Mulligan, 2004; Müller[a] *et al.*, 2007), with bacteria being the most dominant. Their respective concentrations depend on soil type, pH, moisture content, concentration of organic matter and other environmental factors. The vast majority of microbes live in the uppermost parts of the soil, which is shown in Table 3.

Tab.3. Changes in the Concentration of Microorganisms with Depth for a Typical Mineral Soil (Alexander, 1977)

Depth	Organisms/gram of soil [thousands]				
m	Aerobic	Anaerobic	Actinomycetes	Fungi	Algae
0.03-0.08	7,800	1,950	2,080	119	25
0.20-0.25	1,800	379	245	50	5
0.35-0.40	472	98	49	14	0.5
0.65-0.75	10	1	5	6	0.1
1.35-1.45	1	0.4	-	3	-

If a chemical leaches below the root zone, it encounters far fewer microbes and is less likely to degrade before leaching to groundwater. Thus, half-lives in subsoils are usually much longer than those for the root zone because of the great reduction in microbial populations and the changes in physical and chemical conditions. Once a contaminant gets into groundwater, therefore, its degradation is likely to continue at a slower rate.

Aerobic vs. Anaerobic Degradation

Degradation will be usually slower under anaerobic than under aerobic conditions (Fig. 14). This is because**,** aerobic processes generally yield a much greater potential energy yield for bacterial growth and thus aerobic processes tend to occur much more rapidly. However, it has been reviewed by Farhadian et al (2007) that in \`in situ´ bioremediation, anaerobic biodegradation plays a more important role than that of aerobic processes. It has been reported that enhanced anaerobic bioremediation was already successfully applied in some areas contaminated with oil products and that anaerobic processes have advantages such as low biomass production and good electron acceptor availability. Beside, anaerobic processes are sometimes the only probable solution to eliminate pollutants as it is often difficult to inject oxygen into underground waters.

Toxicity of the contaminants

One of the major limitations to biological degradation is the limited growth and activity of most microorganisms in toxic environments (Alexander, 1999; Bressler & Gray, 2003; Warren *et al.*, 2003).
As most contaminated sites contain a wide range of contaminants, it has to be considered, that some of them might exhibit significant toxicities. In many cases these additional contaminants are not well considered and the effect they will have on the biodegradation is not known.
However, as addressed before, a high octanol-water coefficient indicates favored partition from water to biological membranes and increased membrane toxicity. It has been reviewed by Sikkema (1995) and Ramos *et al.* (2002) that the partition to cellular membranes is most preferred when Kow is between 1.5- 4.0. According to Bressler & Gray (2003), compounds with log Kow values in this range, tend to give the highest rates of aerobic and anaerobic biodegradation (Fig.15).

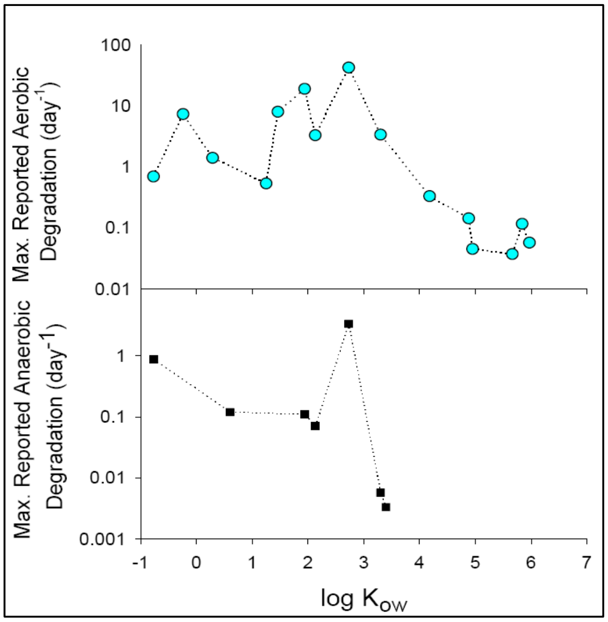


Fig. 15: Correlation of reported maximum aerobic biodegradation rates for known environmental contaminants to their octanol-water partition coefficients. The data taken from a variety of microcosm studies illustrates the main trends in rates of microbial degradation. The maximum rates of aerobic biodegradation are usually an order of magnitude greater than the anaerobic rates. Compounds with intermediate values of log Kow, in the range of 1-3.5, tend to give the highest rates of aerobic and anaerobic biodegradation (Bressler & Gray, 2003).

Bioavailability of the contaminants and time dependent degradation

In order to degrade an organic contaminant the degrading microbe needs (1) a contact with the contaminant, and (2) time for the adaption and/or degradation (Reid *et al.*, 2000; Semple *et al.* 2003). Thus, biological degradation strongly interacts with sorption and transport processes. Both, strong adsorption (Fig. 15) and rapid leaching will presumably decrease the rate and extent of degradation of an organic contaminant (Rockne & Reddy, 2003; Müller^{a} *et al.*, 2007).

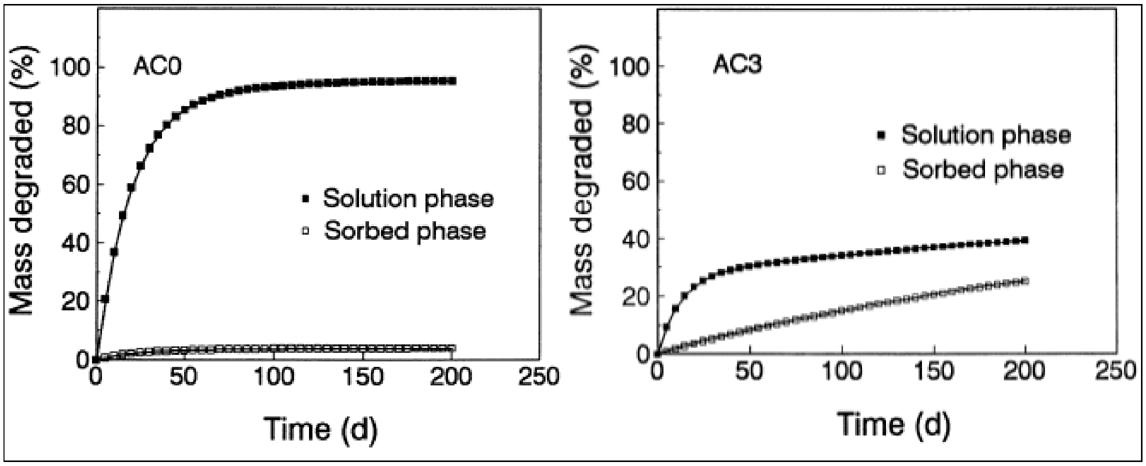


Fig. 15: Comparison of total 2, 4-D degradation in the liquid vs. sorbed phases for activated carbon (AC) concentrations of 0 (AC0) and 2050 (AC3) AC µg g^{-1} soil and for the initial condition that no chemical is partitioned to kinetic sorption sites. The adsorption coefficients increased at higher AC, and were negatively related to degradation, implying that degradation is faster from the liquid phase than from the sorbed phase. Over the long term, degradation will decrease when desorption kinetics becomes the limiting factor (Guo *et al.*, 2000).

It is known that especially, in weathered/ aged contaminated sites, the residual contaminants tend to have low Henry's constants (KH), high octanol-water coefficients (Kow) and high soil organic carbon-water partition coefficients (Koc). Because biodegradation relies on aqueous phase properties, bioavailability is restricted severely in weathered contaminated sites. In some instances, the sorbed fraction of the organic contaminants may also become totally resistant to microbial metabolism.

Effect of Soil Temperature

Temperature is a significant parameter that can influence the equilibriums and rates of environmental processes. For instance, it has been reviewed that increasing temperature decreases the equilibrium sorption of most compounds (Hulscher & Cornelissen, 1996) and results in higher volatilization and leaching losses (VanRoon *et al.*, 2005). Soil temperature is also known to affect microbial activity and contaminant half-life. This is mainly due to the restricted temperature ranges in which they are able to metabolize and grow. Temperature has therefore a great effect on the distribution of the contaminants and the efficacy of biodegradation and also bioremediation processes. Paraiba *et al.* (2003) also recommended the inclusion of soil temperature to calculations of leaching potential indexes which are frequently used as a screening indicator in pesticide groundwater contamination studies.

In summary

For a given contaminant, the pathways and rates of microbial degradation will depend on a wide range of factors. These factors can contribute to either physical or metabolic limitations to degradation. Especially the complex cellular transport processes are not well understood and thus, biological degradation is difficult to predict (Bressler & Gray, 2003).

For Further Reading:
The most comprehensive literature currently available on this topic is: Neilson & Allard (2008) “Environmental Degradation and Transformation of Organic Chemicals”. More detailed information on the abundance and diversity of microbes in the soil and environmental factors that influence soil microbes and biodegradation processes can be found, for example, in a review from Holden & Frierer (2005) or, for instance in several articles in the journal "Biodegradation" (http://www.springerlink.com/content/102854/?sortorder=asc&p_o=0).

3.1.7. Remediation strategies

Soil contamination is a widespread problem that exhibits a serious threat for groundwater quality. Only in Germany, there are approximately 360.000 contaminated hazardous waste sites and up to now not more than 55.000 have been evaluated in terms of their potential for groundwater contamination (Umweltbundesamt, 2003). Generally a wide variety of techniques can be applied for the remediation of sites contaminated with organic pollutants. These techniques can be divided into two categories, `ex situ´ and `in situ´ technologies, as shown in Figure 17 (see also chapters 4.2.1.1 and 4.4).

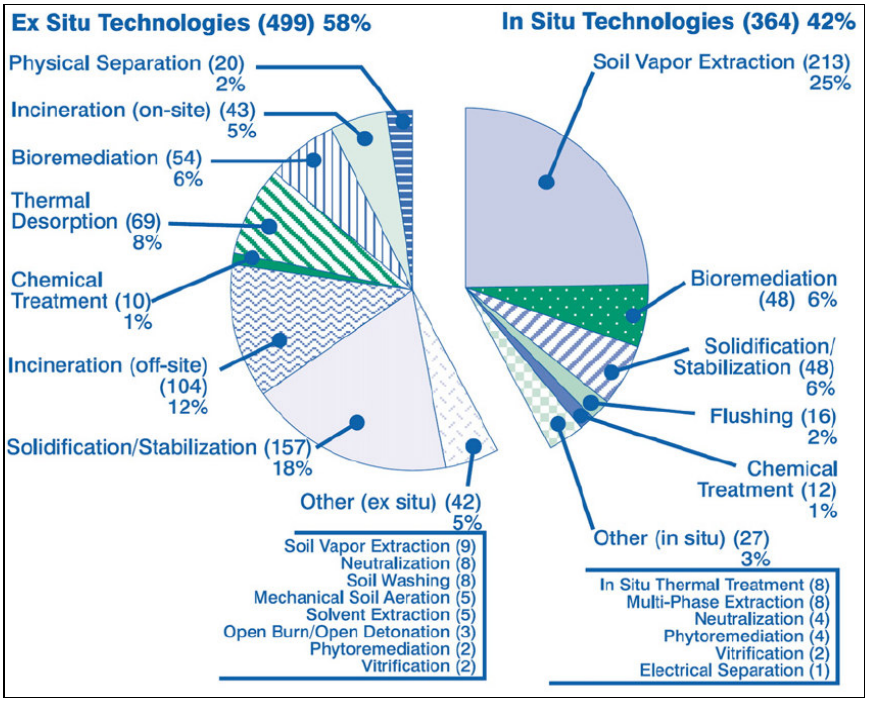


Fig. 17: Technologies selected for source control at superfund remedial action sites from 1982–2002 (Paria, 2008).

The applicability and specific advantage of each method depends on a number of aspects. Generally, certain soils respond better to particular remediation techniques. For instance, if the soils on a contaminated site are primarily sandy, then remediation methods such as vacuum extraction or bioremediation might be suitable depending on the type of contaminant. In contrast, if the soil is fine grained and has a high clay content, then excavation and disposal, thermal desorption or incineration may be better fitting to the task. The location of the contamination relative to surface features, such as buildings, may limit the range of applicable techniques. But even for such a case, promising approaches such as the employment of electro-bioremediation, a hybrid technology of bioremediation and electrokinetics for the treatment of soil reviewed by Wick & Harms (2007) were made. If the contamination is situated at or below the water table, then combined techniques (vacuum extraction, air sparging and pump-and-treat) might be necessary to achieve the remediation. The applicability of the different remediation methods is also dependent on the contaminants. For example, bioremediation will be ineffective for strongly sorbed and toxic contaminants or for contaminant molecules, which are too large to enter the microbial cell (Yong & Mulligan, 2004). (See also chapter

3.1.7.1. Remediation strategies on local scale

Hazard identification and treatability study

The first step in any remediation process is the proper analysis and identification of the contamination problem, both its exact nature and extent. According to Paria (2008) the following information's are necessary to characterize a site: (1) Site geology and hydrogeology, (2) Hydraulic conductivity of soil, (3) Soil type, composition vs. depth, and characterization of the aquifer material (grain size distribution and organic carbon content, (4) Soil chemistry, (5) extent of soil contamination (vertical and horizontal profiles, (6) Total amount of contaminated soil to be treated, (7) Range, concentration, and variability of contaminants in the soil, and (8) History, process, and time frame of the conditions leading to the contamination (see also chapter 4.4.3).

Once the extent of the problem has been identified, the next stage will be the development of a remediation plan which includes a feasibility analysis. Treatability or feasibility studies are used to determine the most technically feasible and cost effective method for remediating a particular site. Consequently this will help to take the right decisions.

For further reading:
Scientific and technical guidance documents for the remediation of contaminated soils from the New Jersey Department of Environmental Protection.
(**http://www.state.nj.us/dep/srp/regs/guidance.htm**)

3.1.7.2. Bioremediation

Although, several techniques are available to manage and control contaminated sites, the costs for the evaluation and remediation of contaminated sites often reach such proportions that remediation can not be afforded. Among all remediation technologies, bioremediation appears to be an efficient and economical process and environmentally sound approach. Intrinsic bioremediation is an environmental site management approach that relies on naturally occurring microbial processes without the engineered delivery of nutrients, electron acceptors or other stimulants. However, the knowledge about the natural limitation has led to structured approaches to accelerate the natural processes. The role of assisted natural remediation in environmental cleanup has been reviewed by Adriano *et al.* (2004).

The key approach to manage pollutants in soil is (1) to profit from the ability of soil microorganisms to degrade these compounds and (2) to accelerate the natural processes and enhance the degradation rate (see also chapter 3.3.6.11).

Acceleration of Natural Processes

The enhanced bioremediation could involve the estimation of optimum environmental conditions for microbial growth (temperature, moisture, pH, salinity etc.), the addition of electron acceptors and nutrients to stimulate microbial activity, and the assignment of selected or modified organisms with enhanced degradation capacity.

Water supply

Water serves as the transport medium through which nutrients and organic constituents pass into the microbial cell and metabolic waste products pass out of the cell. A sufficient moisture level is therefore important to ensure a suitable biodegradation in soils.

Estimation of pH

Most microbes prefer a pH range of 6-9. Beside, the pH affects the solubility, and consequently the availability of many soil constituents, which can affect biological activity. For instance, many metals that are potentially toxic to microorganisms are insoluble at elevated pH; therefore, elevating the pH of the treatment system can reduce the risk of poisoning the microorganisms and support their growth.

Nutrient amendments

If nutrients are not available in sufficient amounts, microbial activity will stop. Nutrients required for cell growth are nitrogen, phosphorous, potassium, sulphur, magnesium, calcium, manganese, iron, zinc, and copper. Enhanced degradation can be realized by providing macro nutrients (nitrogen and phosphorus), micro nutrients (Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}). Nitrogen and phosphorous are the nutrients most likely to be deficient in the contaminated environment and can be added to the bioremediation system in a useable form (e.g., as ammonium for nitrogen and as phosphate for phosphorous).

Injection of electron acceptors

Electron acceptors can be injected alone, or in combination with other activating compounds. Oxygen is the main electron acceptor for aerobic bioprocesses. As a result, various methods such as air sparging, injection of oxygen-releasing compounds (hydrogen peroxide, magnesium peroxide) and trapped gas phase have been used to increase dissolved oxygen concentrations in ground water. Important electron acceptors that are used to accelerate the rate of anaerobic biodegradation are chemical components such as Fe^{3+}, nitrate and sulphate. It has been reviewed by Husain & Husain (2008) that the presence of certain redox mediators enhanced the range of substrates and efficiency of degradation of recalcitrant organic pollutants by severalfold. Additionally, the use of enzyme-redox mediator systems certainly will enhance the chances of remediation and waste water treatment.

Bioaugmentation

Bioaugmentation involves the use of cultures that have been specially bred for degradation of a variety of contaminants and sometimes for survival under unusually cruel environmental conditions. Sometimes microorganisms from the remediation site are collected, separately cultured, and returned to the site as a means of rapidly increasing the microorganism population at the site. In some situations different microorganisms may be added at different stages of the remediation process because the contaminants in abundance change as the degradation proceeds.
Literature on possible degradation methods continuously increase and a comparison of all data became more and more difficult both for a single organic compound and for different ones based on the same or different active principles. Here, the design of a database coupled to suitable expert system software should be strongly suggested (Sammartino *et al.*, 2008).

Enhancing the extractability or bioavailability

It has been reviewed by Saichek & Reddy (2005) and Wick *et al.* (2007) that better contaminant bioavailability can be achieved by employing electro-bioremediation, a hybrid technology of bioremediation and electrokinetics that enables faster contaminant transport to the bacteria or by mobilizing the bacteria. It can be used in situ and is particularly effective in saturated and unsaturated fine-grained soils of low hydraulic conductivity, which are normally difficult to treat by other in situ methods.
Since water solubility of many organic contaminants is the often a crucial point, surfactants can be used to enhance the extraction efficiency or to increase the bioavailability as reviewed by Haigh (1996), Mulligan *et al.* (2001) and Sanchez-Martin *et al.* (2006, 2008).
Cationic, anionic and non-ionic surfactants are useful in displacing dense nonaqueous phase liquids (DNAPL) by reducing interfacial tension between DNAPL and groundwater. By overcoming these capillary forces, the contaminant can be mobilized and finally recovered in extraction wells (Fig. 18).

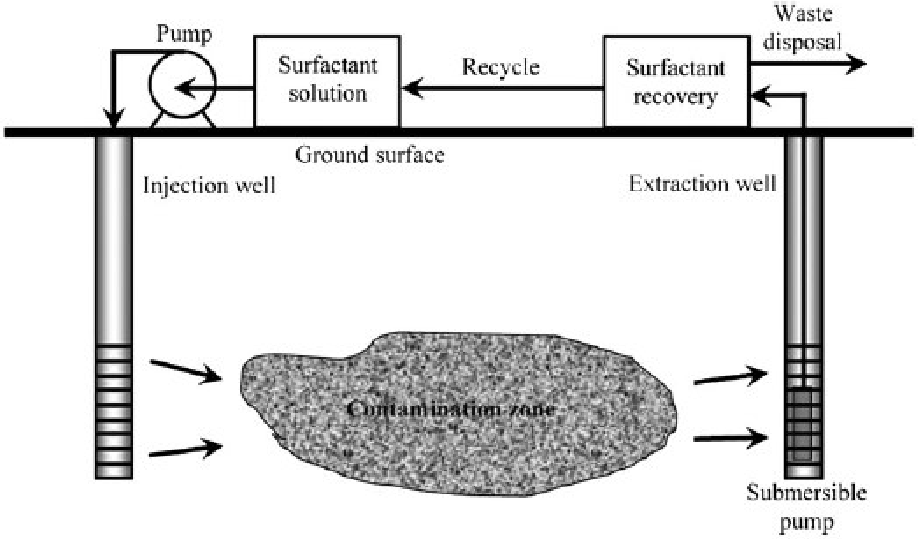


Fig. 18: General scheme of the pump and treat method for remediation of a contaminated site (Paria, 2008).

The main factors that should be considered when selecting surfactants include: effectiveness, cost, and environmental-friendliness. In addition, despite these factors the mineralogy of the subsurface material is quiet important and must be considered Sanchez-Martin *et al.* (2008). A review from Mulligan *et al.*, (2001) provides an overview of the laboratory research, field demonstration and full-scale application of biosurfactants for the remediation of contaminated soil. Synthetic surfactants also biosurfactants produced extracellular as a part of the cell membrane by bacteria, yeasts and fungi are available at low cost and might have promising properties (Mulligan, 2005).

3.1.8. Effects of Climate Change on the fate of organic contaminants

The major environmental issues of concern to policy-makers are the increased susceptibility of ground water quality and the sustainability of natural resources for future generations. To understand the sustainability of the natural resources such as water in general, one needs to understand the impact of climate change and future land use changes on the environmental resources.

It is generally expected that climate changes will affect the behavior and distribution of organic contaminants. Direct effects of climate change, like temperature increase, modification of wind and precipitation patterns, sea level rise, snow and ice cover, may be very effective in altering the partitioning of organic contaminants among the environmental compartments. Other consequences of future climate scenarios may also imply the alteration of degradation rates, soil properties (and hence land use), air-particle partitioning of chemicals and so forth. A case study presented from DallaValle *et al.* (2007) illustrates the major implications of climate change by application of a dynamic multimedia model to show the effects of climate change on the distribution and fluxes of selected polychlorierte biphenyl (PCB) and polychlorierte dibenzofurane (PCDF) congeners over the next 50 y in the Venice Lagoon (Italy). Their model result suggest that if global warming may have the potential of reducing the environmental levels of these chemicals, it would probably enhance their mobility and hence their potential for long range atmospheric transport. This may result in a greater transfer to Polar Regions, where degradation and removal from the environment is more difficult for such chemicals, causing an increase in bioaccumulation and biomagnifications.

From Bloomfield *et al.* (2006) it has been reviewed that the main climate drivers for changing pesticide fate and behavior are changing rainfall patterns (changes in seasonality and intensity) and increased temperatures. The overall effect of climate change on pesticide fate and transport was found to be very variable and difficult to predict because of: (1) the uncertainties associated with the climate predictions, (2) the complexity of the natural environment and, (3) most importantly, because of the range of competing climate-sensitive processes that may have conflicting implications for contaminant fate and transport.

In the long term, land-use changes driven by changes in climate is thought to have a more significant effect on pesticides in the environment than the direct impacts of climate change on specific pesticide fate and transport processes (see also chapter 4.6).

3.1.9. Innovative materials for the removal of organic contaminants

Currently research has focused on the development of low cost and highly reactive innovative materials. These modified natural or designed materials can be very useful in treating aqueous systems, including wastewater and aqueous waste streams, by removing undesired substances. In addition, it might be possible to incorporate or inject these materials into soil and subsoil, in order to enhance the sorption and retention of organic contaminants. Promising materials are for instance:

Granular Activated Carbon

Granular activated carbon is a highly porous adsorbent material, produced by heating of organic matter in the absence of air. From Koelmans *et al.* (2006) it has been reviewed that black carbon may strongly reduce the risk posed by organic contaminants in sediments and soils. They identified that increased sorption is general, but strongest for planar (most toxic) compounds at environmentally relevant, low aqueous concentrations.

The efficiency of two types of activated carbon for the removal of two representative pharmaceutically active compounds (PhACs) (naproxen and carbamazepine) and one endocrine disrupting compound (nonylphenol) from water has already been shown from Yu *et al.* (2008). However, the widespread use of commercial activated carbon is sometimes restricted due to high associated costs. To decrease treatment costs, attempts have been made to find inexpensive alternative activated carbon (AC) precursors, such as waste materials. A review on the preparation of AC by recycling different types of waste materials and also to its application in various aqueous-phase treatments is available from Dias *et al.* (2007).

Organo-clays

Natural clay minerals have a drawback in the sense that they contain inorganic cations which, in aqueous medium, are strongly hydrated, and confer their surface a hydrophilic character. Thus, they are good adsorbents for cationic compounds but not for anionic, and non-ionic/ hydrophobic organic compounds, such as most pesticides (Cox *et al.*, 1997; Sanchez-Martin *et al.*, 2006).

Nevertheless, among the different materials, the use of clay minerals has been subjected to considerable attention due to their low cost, ubiquitous occurrence in nature and the possibility of modifying their surfaces to improve their affinity for specific contaminants (Lagaly, 2001, Celis *et al.*, 2002 and Hermosin *et al.*, 2006). Research has also focused on the ability of unaltered and modified clay. Unaltered and modified clay minerals have also been proposed, alone or mixed with soil, as reactive barriers to reduce pesticide leaching in soil and to minimize the risk of ground water contamination (Undabeytia *et al.*, 2000, Nennemann *et al.*, 2001, Sanchez-Martin *et al.*, (2006) and Rodríguez-Cruz *et al.*, 2007).

Biosorption

the usage of untreated (live) or treated (chemical or heat treated) microorganisms as biological adsorbents has attracted attention and might be a promising alternative to replace or supplement the present removal processes of organic pollutants including dyes, phenolics and pesticides from wastewaters. The usage of inactive microorganisms and the parameters affecting the biosorption rate and capacity has been reviewed in detail by Aksu (2005).

Improved techniques for drinking water treatment and wastewater treatment

Pharmaceuticals and unmetabolized drugs are excreted in faeces and urine (human and animal) and may be released from hospital and medical centre disposal. Finally they will reach sewage treatment plants, which are not necessarily designed to remove these substances from the waste stream. Same problem originates from Personal Care Products, which are designed to be non-toxic but some contain endocrine disruptors. Until now, little attention has been directed to this problem. Recently the efficiencies of conventional drinking-water-treatment process in removal of pharmaceuticals and other organic compounds were subject to a study from Stackelberg *et al.* (2007). They analyzed water and sediment samples from a conventional drinking-water-treatment (DWT) for 113 organic compounds. The results showed that the effectiveness of the treatments varied widely within and among classes of compounds. But the detection of 21 of the compounds in 1 or more samples of finished water, and of 3 to 13 compounds in every finished-water sample, indicates substantial but incomplete degradation or removal of organic contaminants through the conventional DWT process used at this plant.

These results are generally alarming, as the risks of long time exposure are mainly unknown.

The study from Gultekin & Ince (2007) provides an overview of the literature on classes and types of compound described as “endocrine disruptors” and their treatability in water by advanced oxidation processes, which generate hydroxyl radicals in water. Focus on the destruction of bisphenols, alkylphenols and phthalates which are among the most highly suspected endocrine disrupting compounds.

3.1.10. Conclusions

The literature dealing with the retention, transport and degradation of organic contaminants in soil and groundwater has been reviewed. The review covers a wide range of issues relevant to the understanding of the mobility of organic contaminants in soil and groundwater systems. Most results have been derived from controlled laboratory experiments. From these studies it can be concluded that operative mechanisms for any particular interaction between contaminants, soil constituents and soil biota depends on the nature and properties of the soil surfaces, the chemistry of the system (e.g. pH, kind of exchangeable cations, water saturation degree) and the chemical nature of the organic contaminant.

The main mechanisms, which are essential for the development of management strategies (immobilization, mobilization and remediation), are relatively well understood. Nevertheless, in many cases it seems not clear; if or how results from controlled laboratory investigations can be up-scaled and applied to heterogeneous and transient field situations. Today, most discreet organic chemicals are measurable by sophisticated instrumental methods, and procedures are available to assess exposure risks in many cases. The evaluation of physico-chemical and toxicological properties and the regulation of chemicals, especially with high production volume, is of primary importance to avoid contaminations and related risks.

The modification of soil parameters in order to reduce contaminant leaching, enhance sorption and degradation is generally possible, but because of the unique properties of each contaminated site there might be limitations in generalization of management strategies. Relevant parameters must be well characterized because otherwise they may cause negative effects on the environment. The results indicate that future research must take into account multiple management interactions in devising process-based predictions of management effects. Interactions with landscape factors must also be considered explicitly. A successful programme will require integrated input from soil scientists, engineers, chemists and microbiologists.

There is little doubt that even relatively modest climate alterations will bring significant environmental changes. Chemical cycles will be also affected in a variety of ways, and the interaction between climate impacts and the possible adaptation/mitigation options that will be adopted will increase the uncertainties. The main problem in applying the climate change scenarios in a research context is the present lack of understanding of the complex interdependencies of climate-sensitive processes in the environment and the uncertainties associated with the effects of climate change on economic and social factors.

3.2 Deltares-TNO: Literature review

The role of Soil Organic Matter composition in Organic Contaminant retention

3.2.1 The role of Soil Organic Matter composition in Organic Contaminant retention

In the persistence of organic contaminants in soil systems, soil organic matter plays a crucial role. For the sorption behavior of a particular organic contaminant, with a relatively well known set of characteristics, the content and variability in soil organic matter composition varies depending on location and is a decisive factor. Soil organic matter (SOM) principally consists of plants and animal-derived detritus or their degradation products, as well as more condensed forms of organic matter, such as kerogen, coal, soot, charcoal, and black carbon. Whereas fresh soil organic matter tends to be highly reactive toward ionic and polar contaminants because of ionisable functional groups within natural organic matter such as carboxylic and phosphate moieties. With continued degradation, most of these functional groups are lost, resulting in more condensed organic structures. In addition to these, thermally altered and geologic forms of organic matter, are the main sorbents for non-polar, more hydrophic contaminants, as will be discussed in this section (see also chapters 3.1.4.1, 3.1.3.2 and 4.5).

Sorption by organic matter occurs by absorption into amorphous organic matter as well as by adsorption onto hard carbon, such as kerogen, soot, or black carbon (Cornelissen *et al.*, 2005; Koelmans *et al.*, 2006). Transformations to the chemical composition of the organic matter are caused by various physical, chemical, and biological processes. For example, soil organic matter becomes more aromatic in character with time as continues diagenesis further degrades plant material. This greater aromaticity of natural organic matter results in greater sorption capacity for hydrophobic organic contaminants. Grathwohl (1990) demonstrated that the sorption capacity of soil constituents is related to the age of the soil organic matter. Likewise, simulated diagenesis of peat has shown that aged peat had increased sorption capacity for phenanthrene (Johnson *et al.*, 2001).

For a mechanistic understanding, much of the fundamental research has so far focused on isolated simple sorbent models (e.g. peat or soot), not integrating the contributions from various compound classes with soil organic matter. This is important since different types of solid organic carbon retain hydrophobic organic contaminants to different degrees. In particular, coal-derived, soot and other black carbon materials have almost two orders of magnitude higher sorption capacities compared to degraded plant materials that are endogenously formed in soil systems (Karapanagioti *et al.*, 2000, Grathwohl *et al.*, 1990; Gustafsson *et al.*, 1997; Huang *et al.*, 1997). Therefore, even small fractions of these materials in soils may result in a substantial reduction of soil water concentrations by the sorption of organic contaminants. Black carbon (see Fig. 19), a product of combustion/pyrolysis of either vegetation or fossil fuel, has a high affinity towards the sorption of nonpolar organic pollutants and is ubiquitous in soils and sediments (Schmidt and Noack, 2000). Black carbon is condensed and highly aromatic in structure and composition (e.g. Sergides *et al.*, 1987). Because it is extremely resistant to weathering processes, it persists in the environment.

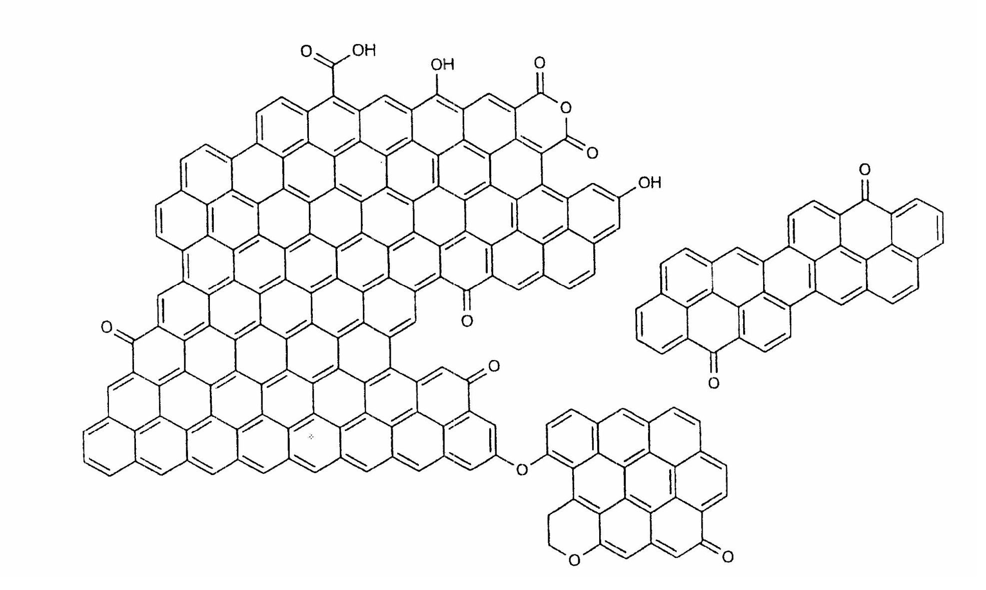


Fig. 19: Schematic black carbon structure (Sergides *et al.*, 1987)

Research so far that focused on the sorption of the bulk soil organic matter, incorporating the influence of all compound SOM compounds, uses empirical models to describe sorption behavior, with fitting parameters for indistinct concepts as HE (very slow desorption domain) and LE (slow desorption domain) sites (e.g. Wang *et al.*, 2005; Kookana and Aylmore, 1993; Lee *et al.*, 1997). Absorption into amorphous organic matter (AOM) is by linear partitioning, for which mainly single parameter models have been used (Doucette, 2003). More recently multiparameter models for the estimation of log K_{oc} values of a variety of compound classes have been developed (Schüürmann *et al.,* 2006; Nguyen *et al.*, 2005) that have increased our mechanistic understanding of organic contaminant-soil organic matter interactions. These models however, were derived from fitting log K_{oc} values for various soils and sediments, that do not take the compositional heterogeneity of natural organic matter composition into account (Schwarzenbach *et al.,* 2003). As such, predictions may be complicated due to the great calibration uncertainty by using the experimental values of K_{OC}, due to the possible contribution of several sorption mechanisms for compounds belonging to different classes. The possibility for reliable prediction of sorption by of organic contaminants by soil organic matter based on its characterization is therefore lacking. Overall the mechanistic understanding of the process of interaction between heterogeneous soil organic matter and organic contaminants, including the variability of soil characteristics at various spatial scales, needs to be further improved to understand and predict their behavior in specific soil systems.

3.3 BOKU: Literature review

Biodegradation of organic pollutants with special focus on glyphosate and AMPA

3.3.1 Biodegradation of organic pollutants in soil and water systems

Biodegradation is the most important mechanism for the removal of organic pollutants from natural environments (van Agteren *et al.*, 1998, Neilson & Allard, 2008). Biodegradation can be defined as biologically catalyzed reduction of the complexity of chemicals which frequently leads to the complete conversion into inorganic products (mineralization) (van Agteren *et al.*, 1998, Pitter & Chudoba, 1990). In biodegradation of anthropogenically and natural pollutants are involved mainly different bacteria and fungi, and to a smaller extent algae, yeasts and protozoa. Microorganisms can exert a large catalytic effect even at low biomass present in sub soils. Rates of degradation in fresh soil sometimes correlate with general properties of microorganisms like respiration, biomass etc (Nicholls, 1991). Manmade organic pollutants are not always as readily degradable by microorganisms as natural organic compounds. There are several definitions of biodegradability in literature (Painter & King, 1985, Alexander, 1965, Gilbert & Watson, 1977, Wuhrmann & Mechsner, 1974). Biodegradability is the ability of an organic substance to undergo microbial attack. Also, biodegradability could be defined as the elimination of an organic compound from an ecosystem by the microbial activity of the biocenosis currently present in this system. We can divide the biodegradation of organic substances into three phases (Alexander, 1965):

1) Primary (functional) - minimum biodegradation which changes the identity of the compound.
2) Environmentally acceptable – degradation leading to the removal of some undesirable compound properties.
3) Ultimate – mineralization of a compound to carbon dioxide, water and additional inorganic compound if elements other than C, H and O are present.

Based on their biodegradability, xenobiotics can be classified as biodegradable, persistent and recalcitrant (van Agteren *et al.*, 1998). The degradation rate is one of the most important factors from the ecological point of view since longer persistence in environment of organic pollutants increases toxicological risk (Pitter & Chudoba, 1990).

The breakdown of complex organic material is characterized by a succession of different microbes with different metabolic capabilities which could explain difficulties in isolating some of the organic pollutant degrading strains (Talaat Balba & Bewley, 1991). Organic pollutant and microbe interaction is mutual, with the mediation of environmental factors. Environmental physico-chemical factors will influence both the microbial degradation of pollutants and also their relative toxicity to the microflora (Talaat Balba & Bewley, 1991). Unlike data for the toxicity of heavy metals and gas pollutants, data of the toxic influence of organic pollutants on environmental microbes are scarcely available. The toxicity of organic pollutants in the soil environment depends on pH, Eh, aeration status, buffering capacity, inorganic anionic and cationic composition, water content, clay mineralogy, hydrous metal oxides, organic matter, cation exchange capacity, temperature, solar radiation, hydrostatic and osmotic pressure (Babich & Stotzky, 1983). In an aquatic environment, the toxicity of similar pollutant concentrations may differfrom that in a terrestrial environment, due to the buffering capacity of soils.

The influence of pollutant toxicity on microbes may be reversible or persistent. It could provoke maximum delay in microbial activity (reversible) or maximum depression (persistent) (Domsch *et al.,* 1983).

Besides toxicity, biodegradability of organic pollutants can be considered a basic factor in determining the behavior of xenobiotics in the environment. Knowledge of biodegradability of organic compounds could adapt the chemical production for better environmental risk assessment (Pitter & Chudoba, 1990).

3.3.2 Factors affecting biodegradation

All factors affecting biodegradation of organic compounds, both natural and manmade, can be divided into those relating to the contaminant and those relating to the environment, even though they are interrelated (see also chapter 3.1.6). Environmental factors may be physical, chemical or biological (Talaat Balba & Bewley, 1991). Besides biodegradation catalyzed by microbes, it is possible for photochemical and other non-enzymatically indiced reactions to take a place in degradation of organic chemicals introduced into the environment, but by contrast to biodegradation rarely lead to total mineralization (Taalat Balba & Bewley, 1991).

3.3.2.1 Factors relating to the contaminant

The biodegradability of man-made chemicals depends on two major factors:

1) The compound structure and degradability by existing microbial enzymes;
2) The compound ability to induce or depress the necessary catabolic enzyme production by microbes;

Xenobiotic can affect biodegradability through:

1) Effects of concentration
2) Chemical structure

Organic pollutant concentration

On one hand, chemical introduction in the environment in large quantities can provoke microbial sterilisation, which can delay biodegradation and make them persistent for longer time than normally (Nichols, 1991). On the other hand, too low concentrations can not support microbial growth (Taalat Balba & Bewley, 1991).

Effect of chemical structure

Chemical structure of xenobiotics can either hinder or favour biodegradation. Slight modification in the molecular structure can make xenobiotics more persistent or more readily biodegradable. The type, number and position of substituent can influence the resistance of the organic compounds (Taalat Balba & Bewley, 1991).

The type of substituent can enhance the resistance of organic compounds if:

1) methyl group(s) substitute hydrogen atoms of mono - and dicarboxylic acids, aliphatic alcohols and alkylbenzenesulphonates;
2) chlorine substitute hydrogen of aliphatic acids;
3) chlorine atoms replace methoxy groups of triazines or methoxychlor;
4) nitro, sulphonate and chloro groups replace carboxyl or hydroxyl of derivates;
5) methylthio or methoxy groups replace chlorine or amino group replace hydroxyl of triazine derivates.

The number of substituents can favour persistence of organic compounds:

1) di- and trichlorobenzoic acid are more resistance than monochlorobenzoic acid:
2) chloroacetic acid, substituted propionic acid, isopropyl-N-phenyl carbamate contaning two instead or one, or sometimes three instead of two chlorine atoms;
3) diaminobenzenes are less available than monoaminobenzenes.

The position of a substituent influences the persistence of different organic compounds. For some chemicals a meta position favours resistance of the xenobiotics and for some others conversely, ortho position makes them more persistent.

There is also a need for more information about different kinds of substitution like replacement of carbon atoms of natural cellulose fibrous by oxygen, sulphur or nitrogen (Taalat Balba & Bewley, 1991).

3.3.2.2 Environmental factors

Environmental factors mediate the mutual interaction between organic pollutants and microorganisms, and thus the biodegradability of xenobiotics in the micro-environment. These factors can be divided into chemical, physical or biological in origin (see also chapter 4.1).

Chemical and physical factors

1) Nutritional supply of carbon, nitrogen and phosphorus can enhance or limit biodegradation of xenobiotics in both water and soil environments (Atlas, 1981). There is a lot of information about the negative influence of leaching nitrogen and phosphorus on the degradation of hydrocarbons (Atlas, 1981, Raymond *et al.*, 1976, Dibble & Bartha, 1979). On the other hand, an alternative carbon source could enhance biodegradation of PCBs (Baxter *et al.*, 1975).
2) Organic carbon content of soil can influence bioavailability due to the sorption of different organic compounds (Nicholls 1990). Bioavailability to microbes of sorbed/bound organic pollutants affects their persistence in soil (O'Loughlin *et al.*, 1988). On the other hand an increase in soil organic content leads to an increase in soil biomass, which implies a complex relationship between rates of degradation and the organic content in soil (Nichols 1990). Organic matter in soils has also been found to increase the rate of biodegradation due to high native microbial and fungi populations (Mackay and Betts, 1991). There is also evidence of stimulatory effects on biodegradation due to sorption of microorganisms to soil solid surfaces which could bring them in close proximity to sorbed organic pollutants (Ogram *et al.,* 1985). In some cases organic pollutants can be coupled to humic material which could protect them against biodegradation as long as the humic material resists to decaying processes (Sims *et al.*, 1991). Anyway, there is a need for more information about the

influence of sorption on biodegradation as well as simultaneous investigation of sorption and desorption effects on organic pollutant bioavailability and biodegradation.

3) Presence of other pollutants not amenable to biological degradation, e.g. heavy metals, could significantly depress biodegradation due to their toxicity for microbes (Taalat Balba & Bewley, 1991).
4) Temperature rise can increase degradation rates (Nicholls, 1990). However, there are indications that this relationship is more complex. Different groups of microorgnisms have a different need for temperature conditions on one hand and on the other hand, temperature can influence solubility or volatilisation of organic pollutants (Pencorbo & Varny, 1986).
5) Soil-water content influences biodegradation due to the moisture influence on microbes on one hand and on the other due to antagonistic relationships with the air content in soil pores. A decrease in water content depresses biological activities in soil (Alexander, 1977).
6) pH influences chemical transformations if they are acid or base catalysed. Moreover, extreme pH conditions in soil affect the structure of the microbial population. Most of the pollutant-degrading microbes prefer pH values from 5 to 7-8. In extreme pH conditions, chemical transformation is favoured (Nicholls, 1990).
7) The presence or absence of oxygen has the most important influence on degradation rate and extent of organic pollutant degradation, due to different aerobic and anaerobic degradation pathways. Soil water and air content depends on soil texture.
    a. Under aerobic condition, microbes will generate energy form oxidation of organic compounds to carbon dioxide. Many of organic pollutants are used as carbon and energy source under aerobic conditions (e.g. hydrocarbons). For aerobic degradation microbes produce different types of oxygenases, i.e. enzymes catalyzing reactions that incorporate molecular oxygen (Van Agteren *et al.*, 1998).
    b. Anaerobic degradation occurs under condition where instead of oxygen some other ions or substances serve as final electron acceptors (reactants). For that purpose microbes can use manganese or iron ions, sulphur, sulphate, nitrate, carbon dioxide, some organic intermediates (fermentation) or pollutants (e.g. tetrachloroethene) (Van Agteren *et al.*, 1998).

Physical contact between microbes and pollutant

Bioavailability of organic pollutant depends on sorption to soil solids. As already mentioned above organic matter and the other soil compounds such as clay or metal oxides can be a sorbent for organic pollutants and therefore influence pollutant bioavailability. Sorption of organic pollutants is influenced through the combination of soil and pollutant characteristics. Pollutant concentration, solubility, charge, lipophilicity, mobility and structure in combination with soil characteristics such as water content, soil texture and chemistry, particle size and the presence of fissures and cavities influence the bioavailability and hence the biodegradation of organic compounds in soils (Van Agteren *et al.*, 1998).

Biotic factors

In contrast to the very well documented physicochemical influence on biodegradation, far less is known about the interactions of pollutant-degrading microbes with other in the soil and water system. A better understanding of these complex interactions could explain some lacks in our knowledge of pollutant biodegradation. There is also a great influence of plants on microbes in the rhizosphere through plant exudates such as carbohydrates, vitamins, amino acids and enzymes (Lynch, 1982; Hsu & Bartha, 1979).

3.3.3 Types of microbial degradation of organic pollutants

Microbes have developed through million of years different catabolism strategies for organic compound degradation. The recent introduction of man-made products in the environment had matched some of these metabolic pathways of microbes, and even more influenced the development of some adaptation to the new substances in the environment (see also chapters 3.1.6.2 and 4.1).

3.3.3.1 Growth linked biodegradation

For their maintenance and growth, microbes use the products of the degradation induced by their enzyme production. The microbial cell must obtain energy to carry out essential biosynthetic reactions for its continued existence, and to enable growth and cell division. The substrate cannot be entirely mineralized to the end products, there is a need for a portion channeled into biosynthesis of essential molecules (Neilson & Allard, 2008). For these purposes microorganisms have developed different enzymatic strategies. Since xenobiotics are not natural organic components in the environment, their structure, as well as microbial adaptation to new substrates will regulate different metabolic pathways.

Use of constitutive enzymes

Xenobiotics which are quite similar to natural organic compounds can be degraded by the use of already present enzymes in microbes. These enzymes, which are always present and necessary for microbial survival in the environment, are constitutive (Taalat Balba & Bewley, 1991).

Enzyme induction

For xenobiotics which are different to natural compounds some new metabolic strategies for their degradation are needed. Some of them can induce the microbial production of necessary enzymes. The enzyme induction mechanism involves the regulatory genes on DNA (deoxyribonucleic acid) chromosomes (Taalat Balba & Bewley, 1991, van Agteren *et al.,* 1998).

3.3.3.2 Co-metabolism

The ability of microorganisms to metabolise compounds which cannot be used as a source of energy and growth, is defined as co-metabolism (Taalat Balba & Bewley, 1991). Many of the microbes will degrade xenobiotics only in the presence of more suitable sources for growth linked biodegradation (Neilson & Allard, 2008).

There are a lot of examples of accelerated herbicide degradation following the application of microbial nutrients (Bull, 1980). Moreover, plant exudates input may be an important source for enhanced microbial activity in co-metabolic degradation. Co-metabolism of different xenobiotics could be based on complex activities of the microbial communities, which could be degradation strategies for different xenobiotics where single strain isolation was so far without success (Taalat Balba & Bewley, 1991, Neilson & Allard, 2008). Co-metabolism can cause problems when toxic products are formed and accumulated (e.g. fungal PAH oxidation and bacterial reduction of DDT). In some cases bound residues could be formed and covalently bound to humic material which can make them much more persistent (van Agteren *et al*., 1998) as already mentioned before.

3.3.3.3 Gene information exchange

Capacity of xenobiotic degradation has been shown to be transmissible at least between members of the same genera, and is mediated by the storing of genetic information in extrachromosomal DNA structures called plasmids. This is an important mechanism of bacterial acquisition and a combination of novel information in nature (Taalat Balba & Bewley, 1991, Neilson & Allard, 2008).

3.3.3.4 Enhancement of pollutant bioavailability

Bioavailability of some organic compounds can be depressed by their insolubility. Some microorganisms can influence the solubility of pollutants due to excretion of an emulsifier, thus makeing them bioavailable (e.g. emulsification of hydrocarbons by Corynebacterium hydrocarboclastus and Acinetobacter calcoaceticus) (Zajic *et al.,* 1974, Goldman *et al.,* 1982).

3.3.4 Biodegradation in groundwater systems

As the fresh water is the most fundamental substance for life there is a great interest in the protection and exploration of water supplying systems. Despite their great importance, water bodies are polluted often due to anthropogenic activities, especially in the last century. The introduction of xenobiotics has dramatically increased the risk of water since there is no counterpart in the bio- and geosphere. Of particular interest are groundwater systems, due to drinking water supply. The environmental transformation and transport of the organic pollutant in the soil depends on substance specific characteristics as well as on the physico-chemical and microbiological characteristics of the soil system (see also chapter 3.1.5).

The transport of the dissolved and particle bound organic pollutants depends on the vertical flux in the water unsaturated zone as well as on the horizontal flux in the water saturated zone (Waren *et al.,* 2003). Since there is a great number of different organic pollutants as well as complex processes affecting their dissipation within the riverine and groundwater systems, chemical and ecotoxicological parameters such as adsorbable organic halogen compounds (AOX), dissolved organic carbon (DOC), chemical oxygen demand (COD) or biochemical oxygen demand (BOD) are used to describe the level of anthropological pollution.

Gaps:

- *There is a need for more detailed information on the molecular level for the better understanding of the contamination of water systems (Nicholls, 1991, Schwarzbauer, 2005).*
- *There is also still a need of a better understanding of the chemical behavior in the subsoil and groundwater as well as information about the microbial degradation in these zones.*

3.3.4.1 Influence of the soil properties

Soil texture and structure influence the leaching of the organic pollutants to the groundwater. In sandy soils due to coarser texture and weak adsorption, mobile contaminants can be completely leached to the water zone. In clay soils, pollutants can be retained in the small pores, adsorbed and only slowly moved by diffusion through the soil. Since organic matter content and microbial presence and activity are small bellow the rizosphere zone, sorption and degradation are weak, but there is a lack of knowledge about the fate of organic pollutants in the subsoil and the groundwater zone (Nicholls, 1991, Schwarzbauer, 2005).

3.3.5 Bioremediation

There are three strategies for bioremediation (see also chapters 3.1.7 and 3.1.7.2):

1) In-situ
2) On-site
3) Off-site

The last two are under more controlled conditions. For all of them the presence of genetically stable microorganisms with a good and verified degradation capacity for specific pollutant (Neils and Allard, 2008) is needed.

3.3.6 Biodegradation of selected organic pollutants: Case study on the fate of the organophosphonate herbicide Glyphosate in soil, sediment and fresh water environments

Organophosphonates are synthetic and biogenic organophosphorus compounds, which contain one or more C-PO(OH)$_2$ groups. These groups have a characteristic covalent carbon to phosphor bond which is very stable with a relative resistance to (bio)degradation. Organophosphonates have a very strong interaction with surfaces. They are highly water soluble, while the phosphonic acids are only sparingly soluble. Organophosphonates are also not volatile and poorly soluble in organic solvents (Nowack, 2002; Ternan *et al.,* 1998). Synthetic organophosphonates are used as chelating agents in the pulp, paper and textile industry, as pesticides, detergents etc. Biogenic organophosphonates are used as antibiotics (Nowack, 2002; Ternan *et al.,* 1998). There is a considerable risk of environmental contamination and ecotoxicity, since more than 20 x 10^3 t are applied every year in Western Europe and the USA. Organophosphonates are found in water systems, soil runoff, soil and food (Ternan *et al.,* 1998).

Glyphosate is an organophosphonate herbicide, one of the most widely applied herbicides on a world wide level, in agriculture, railways, dam protection, surface water systems, urban areas, with increasing importance (Nowack, 2002; Ternan *et al.,* 1998; Baylis, 2000). Glyphosate is a post-emergency non-selective broad spectrum herbicide which blocks the shikimic acid pathway for the biosynthesis of aromatic amino acids in plants, also in some microbes, but not in all soil microoganisms (Haghani K *et al.,* 2007). Glyphosate (N-(phosphomethyl)glycine) is the active principle in Roundup®, a product widely applied in regional agricultural practice (see also chapter 4.5).

Glyphosate itself is an acid, but it is commonly used in salt form, most commonly as isopropylamine salt. It is a polar, highly water soluble substance that forms complexes easily. It binds tightly to the soil particles (Nowack, 2002; Ternan *et al.,* 1998; Baylis, 2000).

Usually the persistence is up to 170 with a usual half life of 45-60 days (Peruzzo *et al.,* 2008), but there were also investigations which showed that half-life could be prolonged up to several years (Carlisle and Trevors, 1978 in Zaranyika and Nyandoro, 1993; Eberbach, 1997). Its main metabolite is AMPA (aminomethylphosphonic acid) (Peruzzo *et al.,* 2008; Locke & Zablotowicz, 2004; Gimsing *et al.,* 2004).

3.3.6.1 Current knowledge of the risk of environmental phosphonates

There is a growing concern about identifying and understanding the mechanisms controlling the fate of chemicals which are used as treatment for non-target organisms and which are a source of environmental contamination, especially of water sources. Since organophosphonates are released into the environment in enormous quantities and among the herbicides glyphosate is the one that is applied most frequently, these pollutants constitute a considerable risk. Better environmental protection by improving management practices regarding the use and release control of these chemicals should be expected. There is a need for more specified pesticide management based on the adaptation of the pesticide type and application rates to the characteristics of the area of application (Nowack, 2002; Ternan *et al.,* 1998; Soulas & Lagacherie, 2001; Warren *et al.* 2003).

Gaps:

- *Overview of the phosphonate chemistry*

⇒ *better assessment of the environmental behavior*
⇒ *better risk assessment for non-target organisms and water resources contamination*

3.3.6.2 Factors and processes affecting the pollutant fate in soil

Little information is available about the relationship between pesticide (also other pollutants) and soil quality. There is a need to assess soil quality with respect to pesticide management with regard to the following issues: (1) defining factors that may affect pesticide dissipation and activity; (2) identifying soil characteristics that may be influenced directly or indirectly by pesticide use;(3) evaluating the influence of soil management on mitigating unintended effects of pesticide (see also chapters 3.1.3 and 3.1.4).

Glyphosate fate and behavior in soil is affected by different soil factors and processes, but depends also on interaction between pesticide and soil under specific local conditions. Generally, the following factors can be stated:

- Adsorption conditions, environmental influence, specific soil parameters, soil microbes' behavior, P availability
- Estimation of time dependent degradation rates and consequently risks involved

(Locke & Zablotowicz, 2004; Soulas & Lagacherie, 2001; Gimsing *et al.,* 2004)

Gaps:

- *Influence of the pollutant concentration on biodegradation*
- *Comprehensive understanding of the mechanisms regulating the pollutants' bioavailability/biodegradation*

3.3.6.3 Ways of dissipation

The environmental fate of pesticide and other xenobiotics is mainly regulated by their behavior in soils. In soils, they are affected by various physico-chemical and biological processes conditioning their dissipation and/or accumulation, and their transfer towards other environmental compartments (water, plant, atmosphere). The understanding and measurement of pesticide retention and degradation are necessary for risk assessment of their persistence and contribution to pollution (Mamy *et al.,* 2005).

Dissipation ways of pollutants in soil can be (see also chapter 3.1.3):

- (Soil-Microbial) Biodegradation => pollutant transformation (deactivation) - metabolites
- Leaching through the soil matrix => groundwater,
- Surface run-off (particulate versus soluble transport) => surface water systems

Dissipation ways are time dependent (e.g. Glyphosate biodegradation at the beginning is generally fast, then slower with enhanced adsorption processes; Glyphosate leaching and surface runoff-risk is bigger with rain immediately after the application, before the plants could adsorb it).

(Eriksson *et al.*, 2007; Peruzzo *et al.,* 2008; Zaranyika and Nyandro, 1993; Siimes *et al.*, 2006)

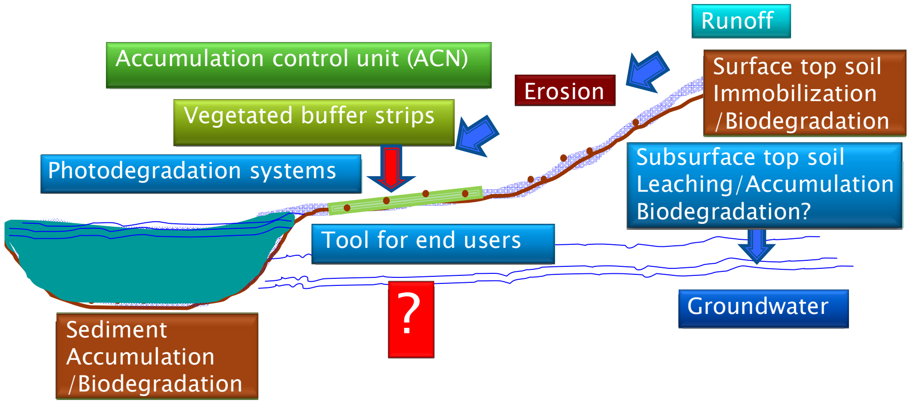


Fig. 20: Dissipation ways of organic pollutants in soil

3.3.6.4 Soil matrix: influence on glyphosate availability

Strong sorption of glyphosate to soil particles may decrease the degradation rate of glyphosate by its reduced bioavailability. Glyphosate can be bound in soil due to (see also chapters 3.1.3.2 and 3.1.4):

- Adsorption on soil colloids
- Adsorpion on Fe/Al-oxides, clays, calcite, organic matter
- Complexation with metals

Availability of glyphosate for decomposition is affected by the rate of desorption. (Eberbach, 1997; Gimsing *et al.*, 2004; Schnurer *et al.*, 2006; Eberbach, 1997; Sørensen *et al.*, 2006; Rodrígez-Cruz *et al.*, 2006; Kools *et al.*, 2005; Ghanem *et al.*, 2007)

Gaps:

- *IEC (Ion Exchange Capacity) for interlayer processes;*
- *Only positive charges? Possible pH /redox influence on glyphosate adsorption/desorption?*
- *Influence of environmental changes on bioavailability of bound glyphosate*
- *Assessment of time dependency of soil bound glyphosate*

3.3.6.5 Soil characteristics: Influence on glyphosate fate

Soil characteristics have great impact on soil processes. Glyphosate fate (dissipation way) as well as other xenobiotics are affected by soil processes through their influence on soil microbial population and activity (see also chapters 3.1.3.2 and 3.1.4). Numerous investigations have shown that the following factors have great influence on pollutant fate in different soils:

- Temperature
- Moisture
- pH
- Aerobic/anaerobic conditions (redox conditions)

(Mamy *et al.*, 2005; Albrechsten *et al.*, 2001; Eberbach, 1997; Blume *et al.*, 2002; Kools *et al.*, 2005; Stenrød M *et al.*, 2005; Stenrød M *et al.*, 2007; Matthies *et al.*, 2008; Fenner *et al.*, 2005)

But there were some studies which, on the contrary, showed that pH had little effect on glyphosate adsorption and biodegradation (Sprankle *et al.*, 1975a, b; Hance, 1976; Moshier and Penner, 1978 in Zaranyika and Nyandro, 1993; Sørensen *et al.*, 2006; Rodrígez-Cruz *et al.*, 2006).

Gaps:

- *Seasonal influence on biodegradation (changes in soil temperature, moisture, aerobic conditions)*
- *Individual and structural microbial response to environmental changes*

3.3.6.6 Biodegradation of glyphosate

Once organophosphonates enter the soil environment, microbial activity has been found to be almost exclusively responsible for their removal (Malik *et al.*, 1989 in Hayes *et al.*, 2000). Biodegradation of an applied pesticide is determined by the soil microorganisms present and by the soil characteristics *in situ* (Tykva, 1998).

Generally microbes and microbial ability for biodegradation are influenced by the type of substrate, temperature, oxygen availability, nutrient supply, similarity of the pollutant to other food sources, previous exposure to the compound or similar ones, and previous environmental conditions which will control the current microbial population (Warren *et al.,* 2003) (see also chapter 3.1.6.2).

Pollutant biodegradation depends also on structural similarity of the pollutant with previously applied compounds. It has already been demonstrated that soil biota can adapt to a new pollutant and even develop the ability to rapidly degrade certain soil-applied xenobiotic when they are similar to already present xenobiotics in soil (Singh *et al.,* 2005; Arbeli and Fuentes, 2007).

Spatial heterogeneity of microbial distribution

There is a considerable spatial heterogeneity in the degradation rate of pollutant and general carbon utilization by microbes even across small areas. This heterogeneity is affected by environmental factors affecting microbial activity and growth. The changes of environmental conditions are influenced by vertically and horizontally depth and topographical redistribution of water, oxygen and organic matter.

There are two scales for spatial heterogeneity of microbial distribution:

- Microscale (spatial colony distribution/pollutant availability)
- Field scale (heterogeneity of environmental characteristics)
-

(Tykva, 1998; Papiernik SK, 2001; Stenrød *et al.,* 2006; Sørensen *et al*., 2006; Rodrígez-Cruz *et al*., 2006; Blume *et al*., 2002)

Gaps:

- *Horizontal and vertical variability of microbial communities/biodegradation*
- *Subsurface biodegradation how deep?*

Soil microbes active in organophosphonate (glyphosate) biodegradation

Consideration of the whole soil biomass in relation to pesticide biodegradation is a poor characteristic. For a complex biodegradation study the isolation of an active constituent of the soil microorganisms present *in situ* is necessary (Tykva, 1998).

- Bacterial strains - (*Pseudomonas* sp., Agrobacter, *Arthrobacter* sp., *Rhizobium meliloti*, Streptomycin, *Escherichia coli*, *Flavobacterium* sp. etc.)
- Fungi – Fusarium (Phytopathogenic, potentially dangerous in the soil environment (Krzysko-Lupicka and Sudol, 2008)), Trichoderma harzianum, *Scopulariopsis* sp., *Aspergilus niger, Geobacillus caldoxylosilyticus* etc.
- Yeasts – (Metal complexes affinity?)
- Marine diazotroph *Trichodesmium*
- Cyanobacetria *Spirulina* spp.
- Actynomycete *Streptomycete* isolates
- Unculturable soil microorganisms

(Tykva, 1998; Gimsing *et al.,* 2004; Foster *et al.,* 2004; Balthazor and Hallas, 1985; Singh *et al.,* 2005; Arbeli and Fuentes, 2007; Dyhrman *et al.,* 2006; Liu *et al.,* 1991; Hayes *et al.*, 2000; McMullan G *et al.,* 1993; Pipke and Amrhein 1988; Kishore and Jacob, 1987; Jacob GS *et al.,* 1988; Lipok *et al.*, 2007; Krzysko-Lupicka *et al.,* 1997; Krzysko-Lupicka and Sudol, 2008; Obojska *et al.,* 1999; Forlani G *et al.,* 1999; Obojska *et al.,* 2002; Dick and Quinn 1995; Vathanomsat and Brown, 2007)

Gaps:

- *Role of unculturable strains and isolation?*
- *Risk from Fusarium?*
- *Involment of yeasts?*
- *Accelerated/stimulated biodegradation?*
- *The role of gene exchange in accelerated biodegradation?*
- *Lag phase?*

Types of microbial biodegradation

Microbial populations are responsible for the vast majority of biotic transformations in the environment. There are five basic types of transformation in which microorganisms are involved:

- Proliferation (growth-linked) biodegradation
- Co-metabolic biodegradation
- Polymerization/conjugation
- Accumulation
- Secondary-effect transformation

(Warren *et al.,* 2003)

In numerous studies glyphosate degradation was observed as co-metabolic process.

(Krzysko-Lupicka and Sudol, 2008; Gimsing *et al.*, 2004)

In some other studies, there was proliferation type microorganism biodegradation of organophosphonates (glyphosate) (Krzysko-Lupicka *et al.,* 1997; Obojska *et al.,* 1999, Dick and Quinn 1995).

Gaps:

- *Better assessment of glyphosate biodegradation type (co-metabolic or proliferation);*

Glyphosate biodegradation pathways

The pathways and rates of microbial degradation in the environment depend on a wide range of factors regulating microbial population, size and ability to metabolize (Warren *et al.,* 2003). Two major mechanisms have been described for the utilization of phosphonates by microorganisms:

- AMPA pathway due to C-N cleavage by oxidoreductase flavoprotein
- Sarcosine pathway due to C-P cleavage => glycine

(Gimsing *et al.,* 2004; Warren *et al.,* 2003; Dyhrman *et al.,* 2006; Hayes *et al.*, 2000; Liu *et al.,* 1991; Rueppel ML *et al.,* 1977; Lipok *et al.*, 2007; Krzysko-Lupicka and Sudol, 2008; Krzysko-Lupicka *et al.,* 1997; Obojska *et al.,* 1999; Forlani G *et al.,* 1999; Obojska *et al.,* 2002; Dick and Quinn 1995)

Gaps:

- *Description of other pathways;*
- *Better assessment of C-P bond cleavage by C-P lyase;*
- *Only P source? C and N is also possible* (McMullan G *et al.,* 1993)*, but more information is needed!*

Glyphosate influence on microbes

The measurement of the total soil microbial biomass (measured as carbon or nitrogen in biomass) is a standardized component of ecotoxicity assessment of the guidelines for pesticide registration of the Organisation for Economic Co-operation and Development (OECD) (Anderson *et al.,* 1992). Unfortunately, measurement of microbial biomass does not provide information about the changes of biodiversity and community structure of soil microbes (Locke & Zablotowicz, 2004).

All xenobiotic pollutants affect the soil microorganisms through their influence on:

- ⇒ Biomass/Activity
- ⇒ Biodiversity/Community structure

In some investigations either no effect of glyphosate on microbial biomass (Haney *et al.,* 2000; Busse *et al.*, 2001), or an increase after application (Haney *et al.,* 2002; Hart & Brooks, 1996; Rueppel ML *et al.,* 1977) could be observed.

Heinonen-tanski *et al*. (1985) and Lupwayi *et al.* (2004) found no effect of glyphosate application on microbial diversity, while Liphadzi et al (2005) found no effect on microbial communities. In the investigation of Charkravarty and Chatarpaul **(**1988), non-target effects on ectomycorhizal fungi were not observed. Results of the study of Levesque and Rahe (1992) have shown that glyphosate inhibits the growth of mycorrhizal fungi and consequently may stimulate the growth of *Fusarium* fungi.

Another study found an influence of glyphosate on soil microbial population and community structure (Gimsing *et al.,* 2004; Sánchez ME *et al.,* 2004; Widenfalk *et al.,* 2007; Araújo *et al*., 2003; Zabaloy MC *et al*., 2008; Ratcliff *et al*., 2006; Johnsen K *et al.,* 2001; Santos and Flores, 1994; Krzysko-Lupicka and Sudol, 2008).

There is also concern about the growing influence of increasingly spreading of transgenic crops (glyphosate resistance). Transgenic crops can affect soil microorganisms due to the difference in amounts and composition of root exudates, gene transfer and different management practices and due to differences in the amounts and composition of decomposing crop residues (Saxena *et al*., 2002; de Vries and Wackernagel, 2004; Sessitsch *et al*., 2004; Motavalli *et al*., 2004; Saxena and Stotscky, 2001; Hopkins and Gregorich, 2005; Accinelli *et al.,* 2004)

Gaps:

- *Ecotoxicological risk for soil microbes (non-target effects e.g. on Bradyrhizobium japonicum);*
- *Shifts in community structure (enhancement of some microbial groups/suppression of others);*
- *Influence on microbe community metabolic complementation and efficiency;*
- *Microbial response on glyphosate concentration/availability;*

3.3.6.7 Indirect effect of glyphosate application on soil properties

Loss of the standing and potential above-ground and below-ground forage biomass because of glyphosate application could account for the relatively short-term differences in organic matter (and microbial and biochemical parameters) and soil structure between the glyphosate and no-glyphosate treated agricultural areas (*Carter et al.,* 2007; Johnsen K *et al*., 2001).

Due to cell reduction of Azotobacter vinelandii and Azotobacter chrococcum, nitrofixation of these microorganisms was also affected (Santos and Flores, 1994).

Gaps:

- *Influence on soil processes due to enhanced changes in microbial communities;*

3.3.6.8 Glyphosate additives

The extreme ecotoxicity of additives and their influence on soil/groundwater/surface water ecosystems has already been shown in different investigations. Possible negative effects on non-target organisms were observed.

Some of the surfactants can increase the risk for injury or even death for humans!

(Mitchell JK *et al.,* 2008; Lee *et al.,* 2008; Krogh KK *et al.,* 2003; Haefs *et al*., 2002)

Gaps:

- *Development and use of alternative, biodegradable additives;*

3.3.6.9 Environmental fate of metabolites

There is still a lack of data for the better understanding of the environmental fate of AMPA. So far, we know that AMPA is slowly degraded as glyphosate, but there are not enough data about AMPA accumulation. Should AMPA be considered as POP? What about other glyphosate metabolites?

(Peruzzo *et al.,* 2008)

Gaps:

- *Better assessment of the metabolites' environmental fate*

3.3.6.10 Transport ways of glyphosate

Pesticide residues in the bottom sediments of the surface water systems may be influenced by a number of factors, including runoff potential and intrinsic properties of the pesticides (Krueger *et al.,* 1999). In some studies, the risk of glyphosate runoff was observed (Eriksson *et al.,* 2007, Warren et al, 2003; Krueger *et al.,* 1999; Peruzzo *et al.,* 2008; Warnemuende *et al.,* 2007; Siimes *et al.*, 2006; Widenfalk *et al.,* 2007). During the process of runoff, glyphosate can be transported as:

- Soluble in runoff water
- Bound to soil solid particles
- Bound to soil aggregates (see also chapters 3.1.5, 3.3.5.1 and 4.2.1.3)

Risk for surface water systems!

On the contrary, in another study, a lack of runoff of glyphosate was observed, probably due to its tight bonding to the soil (Rueppel ML *et al.,* 1977).

Gaps:

- *Determination of trace concentration in natural waters;*
- *Better understanding of the water sediment influence on the pollutant fate in surface water systems;*
- *Particulate or solute transport of pollutants adsorbed on solid particles?*
- *Lack of information about environmental fate in water systems (e.g. influence of redox condition on glyphosate adsorbed on soil particles);*

Influence of glyphosate on shallow aquifer/aquatic/marine ecosystems

The influence of glyphosate on different water organisms in water systems has already been shown in various investigations. There is still a need for more data, for the better understanding of the influence and behavior of glyphosate and its metabolites in water bodies. The interaction of these pollutants with different organisms in water ecosystems should be investigated in more detail (see also chapter 3.1.5):

- In shallow aquifer ecosystems
- In different aquatic ecosystems: influence on plants and microbes
- Influence on marine plants and microbes

(Warren *et al.,* 2003;Feng *et al.,* 1990; Tsui and Chu, 2007; Peruzzo *et al.,* 2008; Amorós *et al.*, 2007; Widenfalk *et al.,* 2007)

Gaps:

- *Risk assessment for aquatic/marine ecosystems;*
- *Biodegradation capacity of aquatic/marine microbes;*

- *Risk assessment of water deposits (e.g. river and marine beaches);*

Leaching-preferential flows

The sources and transport routes of pesticides to groundwater are multifaceted. They can include non-point sources such as agriculture, with pesticide leaching from top soil via:

- Matrix-flow in sandy aquifers
- Preferential flow or macropore flow in eg tills
- Surface water recharge of groundwater through “leaky streams”
- Soil cracks
- Intra-aggregate pores
- Inter-aggregate pores

In certain soils and under different conditions, there is a risk for groundwater contamination! (Albrechsten *et al.,* 2001; Landry *et al.,* 2005; Papiernik SK, 2001; Stenrød M *et al*., 2007). The degradation potential of pesticide is lower in aquifers than in top soil. In the study of Rueppel ML *et al.,* (1977), glyphosate was considered as pesticide class I and therefore to posses no propensity for leaching.

Gaps:

- *Biotransport of glyphosate?*
- *Hypothesis: Floem transport of assimilates*

⇒ *Deposition in root system*
⇒ *Biodegradation*
⇒ *Secondary release from roots at which soil depth?*

3.3.6.11 Possible problem solutions

There is a need for the development of different risk assessment strategies (see also chapters 3.1.5.4, 4.2.1.1, 4.2.2, 4.2.3, 4.4, 4.4.2 and 4.4.3):

- Monitoring systems in the areas of pesticide application
- Improving management practices in the agricultural field areas, to achieve a better risk assessment of:
    - Pollutant leaching/run-off
    - Pollutant biodegradation/adsorption

(Eriksson *et al*., 2007; Crommentuijn *et al.,* 2000; Zablotowicz *et al.,* 2006; Lupwayi *et al*., 2007; Peruzzo *et al.,* 2008; Renaud *et al.,* 2004; Warnemuende *et al.,* 2007; Albrechsten *et al.,* 2001; Papiernik SK, 2001)

Gaps:

- *Development of locally precise management of pesticide application, based on local soil and water characteristics*

Trap systems for pollutants

As was shown in previous investigations on bioremediation technologies, different strategies (Fig. 22) and techniques could also be used for environmental risk mitigation in the case of glyphosate:

- Vegetated buffer strips (vegetated zones between the fields of application and water bodies, and grass-cover under the vine rows (Feng *et al.,* 1990; Landry *et al.,* 2005) (Fig.21)
- Fe/Al oxide-net
- TiO2-Photodegradation (advanced oxidation processes)
- Fe(II)/Fe(III)-Photodegradation (photo fenton reaction)

Gaps:

- *Development and control testing of trap systems with different pollutants under different scenarios;*

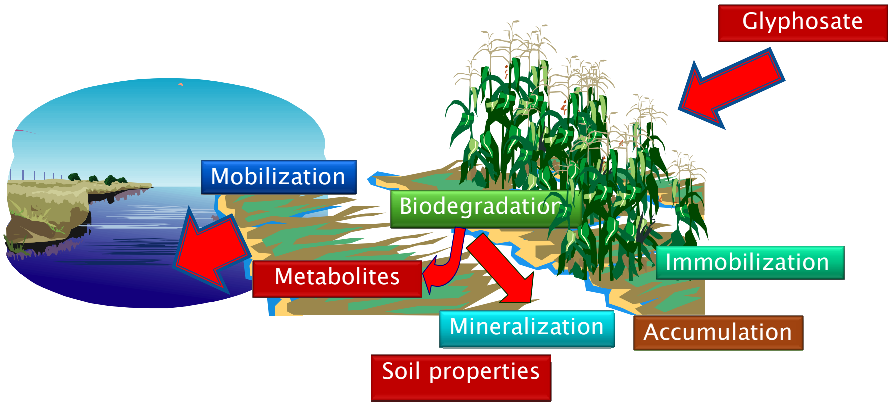


Fig. 21: Vegetation buffer strip – possible trap system for pesticides

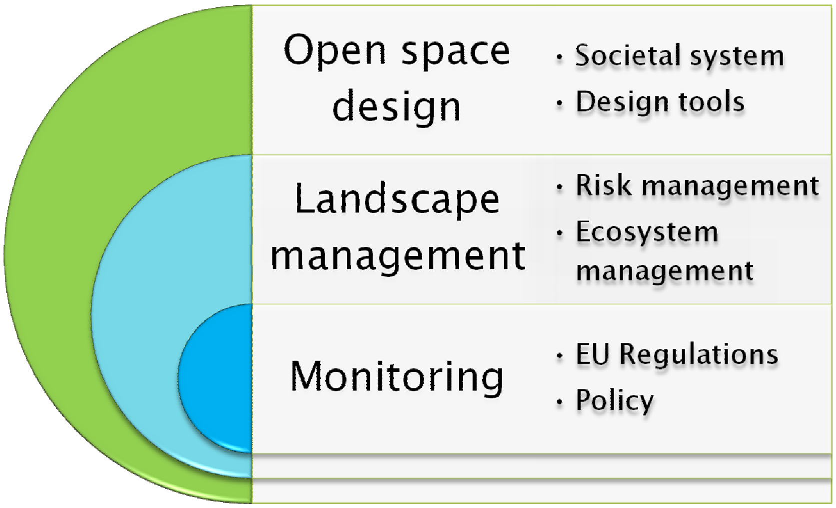


Fig. 22: Possible strategies for organic pollutant mitigation

Enhanced biodegradation

Some studies clearly revealed the possibility for the enhancement of pollutant biodegradation through the use of the following techniques:

- Bioremediation: enhancement of microbial biodegradation through plants (rhizosphere)
- Amendment through the use of:
  - Organic material
  - Urban sludge
  - Isolated microbial strains

(Kadian *et al.,* 2007; Parrish *et al.,* 2005; Dams *et al.,* 2007; Balthazor and Hallas, 1985; Ghanem *et al.,* 2007; Sánchez ME *et al.,* 2004)

Gaps:

- *Development and control testing of different bioremediation systems as well as amendment of different materials for the enhancement of microbial degradation with different pollutants under different scenarios*

3.3.6.12 Multi component analyses of organic pollutants

There is a need for methodological approaches of multi component analyses to measure the trace concentrations in different ecosystems and the rate of pollutant transformation in soil.

- Field measurements - monitoring purposes
- Laboratory measurements - fully controlled

(Crommentuijn *et al.,* 2000; Papiernik SK, 2001)

Gaps:

- *Development of soil extraction techniques for multi component analyses;*
- *Qualitative and quantitative analyses of pollutant multiresidues in soil samples with liquid chromatography (LC);*
- *Development of methods for 80-140 components with liquid chromatography tandem mass spectrometry (LC-MS/MS) and gas chromatography mass spectrometry (GC-MS);*

3.3.6.13 Modeling of soil biodegradation processes

The spreading of different pollutants in the environment depends on interactive, basic physical, chemical and biological processes. Modeling is a powerful approach to obtain a comprehensive understanding of the environmental fate of the pollutants.

Simulation of pollutant behavior in the environment is needed for:

- Research purposes
- Risk assessment (Surface/ground water systems)
- Control and regulation

(Soulas and Lagacherie, 2001; Peruzzo *et al.,* 2008; Matthies *et al.,* 2008; Fomsgaard and Kristensen 1999; Scholtz and Bidleman, 2007)

Gaps:

- *Better assessment of soil biodegradation rate parameters which control the fate of pesticides in soil;*

3.4 UBA-A: Literature review

Emerging pollutants

3.4.1 Emerging pollutants

In literature numerouse substances are identified to be emerging (see chapter 1) and not all of them could be reviewed within this project. Therefore it was decided by all project partners at the first workshop, to focus the literature review on emerging substances on veterinary antibiotics and energetic compounds.

3.4.1.1 Veterinary Antibiotics

The main problem of pharmaceuticals in the environment is the risk of resistances. In human and veterinary medicine a huge amount of antibiotics is in use. This leads to an increase of antibiotic resistances for humans, animals and in the environment (Helmholtz Zentrum München, 2007).

Sources and distribution

There are different sources of pharmaceuticals in the environment (fig.23). One pathway is medicine in the sewage that ends up directly in the soil-groundwater system or in a sewage treatment plant (STP) entering the surface and groundwater in the following. Sewage sludge bears also pharmaceuticals. Another pathway to soil and groundwater is waste in landfill as point source. But the most important path of veterinary pharmaceuticals is the diffuse distribution of manure. Most of the veterinary pharmaceuticals in soils are antibiotics, in particular in regions with high density of livestock. Antibiotics are in use for therapy and prophylactic application on the whole livestock, but also as feed additives (growth promoters). In Europe antibiotics in feed additives are forbidden since 2006.

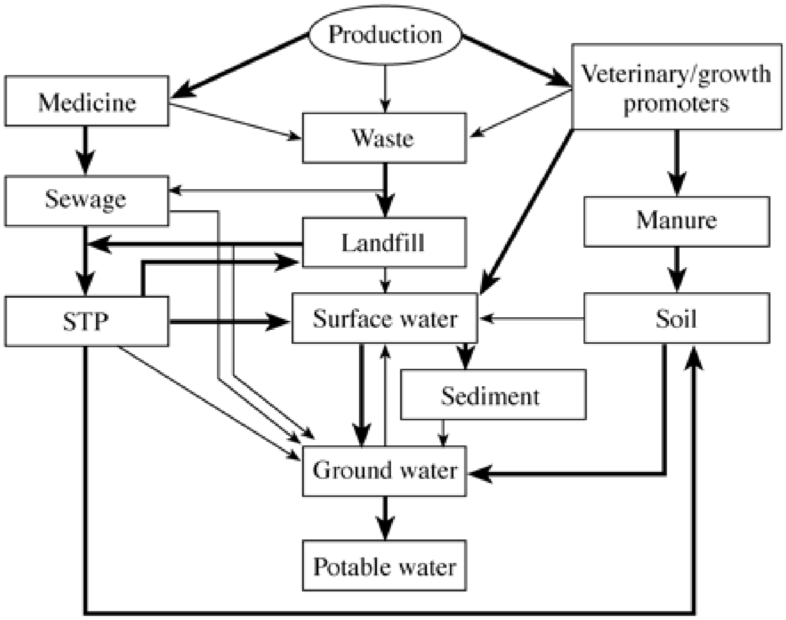


Fig.23: Kümmerer, K.: Significance of antibiotics in the environment. Journal of Antimicrobial Chemotherapy (2003) 52, 5-7 © 2003.

Classification of veterinary antibiotics

Many different veterinary antibiotics are in use. They can be classified by their effect on microorganisms *(EMEA, 1999 - selection)*:

- Blocking of cell wall synthesis (i.e. β-lactams)
- Blocking of protein synthesis (i.e. tetracyclines, macrolides)
- Blocking of nucleic acid synthesis (i.e. sulfonamides)

- Impact on permeability of cytoplasma membrane (i.e. polypeptide antibiotics)

According to the potential effect on microorganisms it is very important to know about the disposition of antibiotics in the environment. Another problem occurs by reuptake of antibiotics in the food chain concerning cross resistances.

Application rate

The application rate of veterinary medicine in Europe in 1997 was estimated by FEDESA (Fédération Européenne de la Santé Animale - European Federation of Animal Health) *(Schwarz, 2001)* at 3.494 tons. This total amount is composed of

tetracyclines	2.294 t (66%)
macrolides	424 t (12%)
β-Lactams	322 t (9%)
aminoglycosides	154 t
fluorochinolones	43 t
sulfonamides	75 t
others	182 t

Other important factors are antibiotic feed additives. The usage in 1997 in Europe was estimated by 1.566 tons.

For comparison the usage of veterinary antibiotics in Germany in 2003 was assumed to be 670 tons in total (SRU, 2007). The main part belonged to tetracyclines, followed by sulfonamides and aminoglycosides. Nearly all of the deployed veterinary antibiotics were used for pigs and poultry (98 %). The SRU (Rates von Sachverständigen für Umweltfragen) assumed an annual usage of 500 tons of antibiotics in human medicine in Germany. Therefore the veterinary amount is one third higher than the human.Similar antibiotic substances are in use for both – veterinary and human medicine. This is the main reason for potential cross resistances.

Until now, only a few different antibiotics could be detected in environment because their values are often below the detection limit and the amounts in use are low. In addition, the detection is only possible with complex analytics. But the most important reason is that old pharmaceuticals are predominant in the environment, which had been approved without any environmental risk assessment. In 1993 the European Agency for the Evaluation of Medicinal Products (EMEA) and a centralized Community authorization procedure were established by Regulation of European Economic Community (EEC) 2309/93. Since 1998 all new antibiotic products in the EU require an environmental risk assessment.

Beyond the concentration of antibiotic substances there is still the question of their behavior in and impact to the environment.

Environmental impact – effect on organisms

The European Medicine Agency established guidelines for environmental risk assessment for veterinary medicinal products. The process is divided into two phases: In phase I the predicted environmental concentration (PEC) of the substance in the environment has to be assessed considering livestock, the composition of the pharmaceutical and the way of application. If the PEC is below the threshold value, the process can be stopped because an environmental impact is not expected. If the PEC exceeds the threshold value, the risk assessment proceeds phase II. Then the PEC has to be evaluated in detail and the predicted no effect concentration (PNEC) has to be assessed. By comparison of exposition and impact a risk quotient can be calculated of PEC/PNEC. If the relation between PEC and PNEC is less than one, the substance can be approved. Otherwise further restrictions need to be fulfilled regarding the protection of the environment or the approval has to be denied (EMEA, 2007; VICH, 2000; VICH, 2005).

Behavior of veterinary antibiotics in the environment

Different factors cause and influence the behavior of veterinary antibiotics in soil and groundwater (Table 4):

- Primarily diffuse contamination by manure (direct deposition by pasture management)
- Biodegradation, sorption capacity, bioaccumulation

- Influencing factors for degradation or sorption (temperature, time of storage, pH-value, light exposure, power of complexation) (SRU, 2007)

Table 4: Behavior in and effect on the environment of different antibiotics (Landesamt für Natur, Umwelt und Verbraucherschutz Nordrhein-Westfalen, 2007 - adapted).

	behavior in the environment		**effect on the environment**	
substance	**relevance**	**requiring further research**	**relevance**	**requiring further research**
Tetracycline	yes	s. single substances	?	s. single substances
Oxytetracyclin	yes	yes	yes	yes
Chlortetracyclin	yes	yes	yes	yes
Tetracyclin	yes	yes	?	yes
Sulfonamide	yes	yes	?	yes
Sulfodimidin	yes	yes	?	yes
Sulfadiazin	?	yes	?	yes
Aminoglycoside	yes	yes	?	yes
Ivermectin	yes	yes	yes	yes

Details in behavior for selected substance groups

Tetracyclines are poorly water soluble and show a high protein affinity. Due to monitoring studies this substance group is highly persistent in soil and barely mobile. Because of the strong sorption on soil particles Tetracyclines are mostly detected in upper soil horizons. By iterative application these substances can accumulate in soil (SRU, 2007).

Concerning **Sulfonamides** less information according to the behavior in the environment is available. These substances were also detected in the groundwater. The estimated persistence in water differs in literature between moderate and highly persistent. By less sorption in soil and a slow degradation they are more mobile and can be transported from agricultural soils down to groundwater (LANUV, 2007; SRU, 2007; Burkhardt, 2006).

The different receptors - soil and groundwater - require a complementary observation!

Present investigations focus on:

- Quantification
- Persistence
- Duration of detection and documentation of decrease in concentration
- Impact on organisms, detection in organisms (bacteria, fish, aquatic plants etc.)
- Effect on functionality of sewage treatment plants by blocking bacteria

By the literature review some gaps could be identified:

- Absence of long term studies
- Verification of antibiotics in soil more difficult than in water – because of sorption on organic matter
- Lack of knowledge of transport, transformation and degradation of antibiotics, specially of sulfonamides (SRU, 2007; Burkhardt, 2006)
    - Abiotic degradation of antibiotics more important than biotic (Thiele-Bruhn, 2004; in SRU, 2007)
- Behavior of metabolites mostly unknown

Considering the application rate and the probably high mobility of Sulfonamides, particularly Sulfadimidin and Sulfadiazin, the number of findings is highly relevant for the environment. But there is still a big demand on research concerning behavior and fate of Sulfonamides in the environment (LANUV, 2007).

3.4.1.2 Energetic compounds

This section gives an overview of energetic compounds in use and their distribution. Furthermore data gaps are identified in the field of their potential risk to the environment.

Beside the manufactured end-products in armaments industry many by-products occurred. Chemical, photolytic and microbial processes in the soil and the water saturated zone led to several secondary metabolites. The result is a chemical mixture in water and soilLots of the verified and suggested substances are hardly detectable in chemical analysis and therefore a substantiated toxicological assessment is still missing (Haas, no time specification).

Classification of explosives (Pennington, 2006)

- Primary explosives
  - extremely sensitive to stimuli such as impact, friction, heat, or electrostatic sources of initiation
- High explosives (secondary explosives)
  - Less sensitive – safe in operation, detonated by primary explosives
  - Trinitrotoluol (TNT), Hexogen (RDX), etc.

Others:

- Propellants (acceleration of projectiles)
- Pyrotechnics
- Waxes and binders
- Smokes

Used to simulate high explosives in military practice rounds

Most important high explosives in World War I, II (Haas, no time specification; Beyer, 2004)

WW I:

2,4,6-Trinitrotoluol (TNT)	202.000 tons
1,3-Dinitrobenzol (DNB)	113.000 t
Picrine acid	52.000 t

WW II :

TNT	20.600 tons/month (in 1945)
RDX (Hexogen)	7.000 t/m
1, 3-Dinitrobenzol	3.300 t/m
Nitropenta	1.390 t/m
Picrine acid	700 t/m

The most problematic substances can be divided in two groups:

- **Aromatic nitro compounds** (TNT, DNB, Picrine acid, etc.)

  - Detectable in ground- and surface water of contaminated sites

- **Nitroamine** (Hexogen, Octogen)
  - Mobile – high distribution in water
  - Heterogeneous distribution in soil

Details in behavior for selected substances

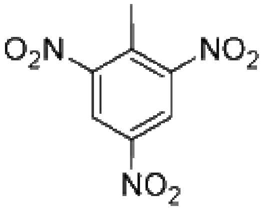
Low risk explosives:

Nitropenta is hardly water soluble (2,1 mg/l) and marginal toxic.

Picrine acid shows high water solubility (12.000 mg/l). It is mostly not detectable in water and soil.

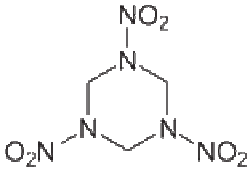
Nitroglycerin is highly water soluble (2.000 mg/l) and volatile. Detection in soil cannot be expected.

2, 4, 6-Trinitrotoluol (TNT) is water soluble (~ 150 mg/l) and persistent in the environment. A threshold value for human toxicity in drinking water is set at 1 µg/l.



TNT is sufficiently investigated, fate and behavior is documented in many publications.

RDX - Royal Demolition explosive (hexogen, cyclonite) is used as brisant explosive or as propellant. RDX is the main component of C4 and Semtex, which were used in civil engineering and mining.



The substance is persistent in environment and its water solubility is estimated at about 50 mg/l. Due to partially microbial degradation intermediates emerge like hydrazine, formaldehyde and methanol (Martinetz, 1996).

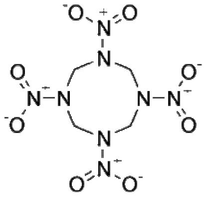
The threshold value for human toxicity in drinking water was determined at 1 µg/l and for ecological toxicity at 50 µg/l (Albrecht, 2004). RDX is carcinogenic and injures central nervous system and digestive organs.

The explosive effect of Royal Demolition explosive reaches 150 % of TNT.

Due to solubility in water and low adsorption on soil particles RDX is highly mobile and probable leads to considerable plumes in groundwater. The loads in groundwater correlate with precipitation. In case of low precipitation an increase in concentration was monitored (Liebig, 2004).

Its heterogeneous distribution in soil makes it difficult to find the emitter (Beyer, 2004).

Cyclotetramethylentetranitramin (Octogen, HMX - High-Molecular-weight, rdX) is a chemical by-product of hexogen. It is supposed to have comparable characteristics like hexogen but there is a lack of investigations.



Distribution

Explosive compounds enter the environment in places of production, storage, disposal and use (Pennington, 2006).

Beside military training areas, former battle grounds and manufacturing areas also civil engineering and mining has to be taken into account.

Of particular interest are the explosive compounds in **unexploded ordnances** (UXO).

> *"UXO are produced when military ordnance fails to detonate or fails to detonate completely. These unexploded projectiles are often difficult to locate, and may be scattered randomly over hundreds of square kilometers. […] They may be physically damaged upon impact, or they may be ruptured from a low-order detonation. Given enough time, they may be penetrated by corrosion. […] This*

> *heterogeneity in physical condition and spatial distribution greatly complicates clean-up and modeling efforts." (Pennington, 2006; p.205)*

RDX from cracked UXO are persistent in upper soil horizons in high concentrations for a long time because of their heterogeneous distributed particles with large surfaces. In spite of the solubility and mobility this results in a long period of groundwater contamination *(Nitschke, 2004).* The corrosion of UXO depends on soil and atmospheric conditions.

According to Pennington (2006) low-order detonations and cracked or ruptured UXO are the main sources of RDX and HMX groundwater contamination in impact areas at military training ranges.

Toxicity of combined pollutants *(Ferreira, 2008)*

Explosives usually consist of different substances like high explosives combined with waxes (i.e. Composition B: 55.2 % RDX, 39 % TNT, 4.8 % HMX, and 1 % wax).

New research suggests that commonly used models in toxicological studies can fail to adequately predict the range of effects of complex mixtures of chemicals in aquatic environments.

There are two different concepts used in the aquatic toxicology for modelling the expected toxicity of individual chemicals:

- Concentration addition (CA)
  - Toxins act in the same manner on organisms and can interact with each other
- Independent action (IA)
  - Each of the toxins in the mixture act differently on the organism without interaction with each other

Conclusion

According to the potential effects of energetic compounds on human, wildlife and environment it is necessary to investigate the behavior of the substances and its by-products. Whereas substances like TNT are immobilized in soil, RDX and HMX end up in groundwater and can contaminate drinking water close to emitters. For sustainable protection of the groundwater the analytical methods for detecting energetic compounds have to be improved and possible stable metabolites have to be identified.

4 Anticipated use and especially application of results

4.1 Influences on the fate of organic pollutants

The ability to take into account the processes that control the overall behavior and fate of organic contaminants in soil systems will allow effective decision making through reliable evaluation of current and future risks. This will be possible to do with confidence when through risk-based management that uses a source-pathway-receptor approach, taking into account site-specific conditions and potential changes to these conditions, such as changes in land use, the receptors present or climate. Obviously, there are many processes, such as degradation and sorption that may change the behavior of organic contaminants in soil systems. Depending on the defined objectives, some of these processes will be regarded as positive or negative. Insight in the main properties of the soil system that control the occurrence and extent of these processes will allow more effective management and anticipation of how future changes to these properties, such as changes in geochemical conditions, affect these processes. We have evaluated the main properties that control the behavior of organic contaminants in various soil processes and have summarized them in Table 5.

Table 5: Evaluation of main properties in soil systems that may affect the mobilistion/immobilisation of organic contaminants in soil systems

Main properties that influence fate		
Organic Contaminant	**Soil and Sediment**	**Environmental**
•Charge^{2} •Hydrophobicity (Koc/w) ^{1,2} •Lipophilicity ^{3} •Molecular weight ^{1,3} •Functional groups ^{1,2,3}	•Clay (%)^{2} •Oxides (%, Fe+Al)^{2} •Organic matter OM (%)^{1,3} •Organic matter (pKa)^{2} •OM composition^{1,3} •Carbonate content (%)^{2,3} •Microbial Mass (%)^{3} •Soil Structure^{1,2,3}	•pH^{2,3} •Eh/redox^{3} •Temperature^{3} •EC^{2} •Water Composition^{2}
Processes that determine fate		
Non-ionic Sorption (1)	**Ionic Sorption (2)**	**Degradation (3)**

From analyzing Table it becomes clear that the properties of the organic contaminant are constants in their behavior in soil systems, with respect to the sorption and degradation processes. No changes occur in their behavior in the soil system, unless changes are made to the input (source) side of the system, such as reduced application or use of alternatives. Within the soil system the environmental properties and those associated with the soil components themselves are variable, on shorter and longer time scales respectively.

For example, with respect to the emerging contaminants discussed in Chapter 3.5, it can be derived that tetracycline is most influenced by non-ionic sorption processes, whereas nitroglycerin is controlled by degradation processes.

Many examples can be given how these various properties influence organic contaminant behavior, and three major types of changes can be identified:

1. Physical changes
2. Chemical changes

3. Biological changes

Physical changes: Such as occurring from human activities (e.g., land use change and associated soil excavation, water table changes) or natural phenomena (e.g., droughts or floods). Depending on the degree of physical disturbance, contaminants that were previously unavailable may become more available or have altered transport pathways, potentially leading to increased exposure to receptors (see chapters 3.1.3.1, 3.1.3.2).

Chemical Changes: Such as changes in pH or ionic strength. This may occur as a result of natural changes (plant growth) or human activities (disposal of waste materials) in the vicinity of contamination. Changes in pH can affect the speciation and consequently the availability of many metals as well as the binding of organic compounds to solids (see chapters 3.1.4 and 3.3.2.2).

Biological Changes: Such as toxicity effects of the pollutant or molecule modification, solubility that suppress biological activity organisms, changes in organic matter and nutrient (N, P) content, redox, temperature, presence/absence of oxygen, and microbial nature (see chapters 3.1.6.2 and 3.3.3).

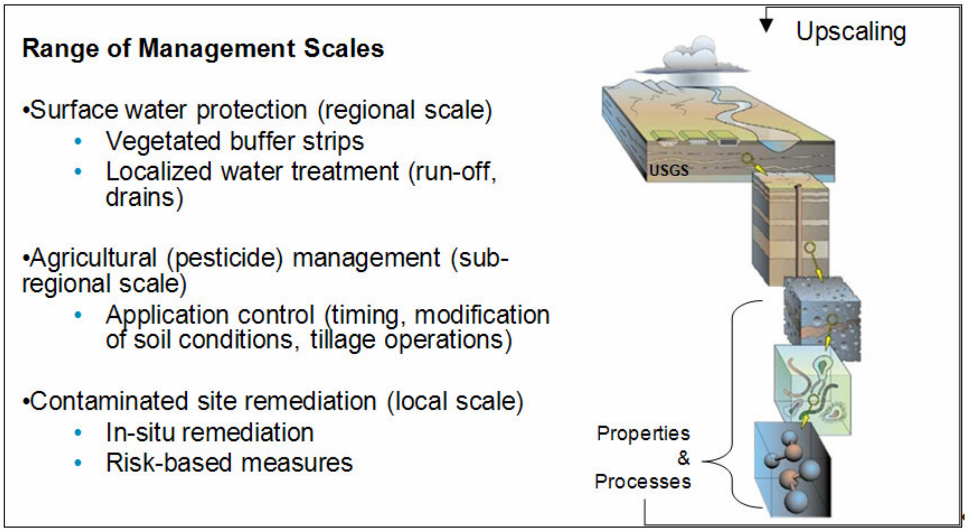
4.2 Management Strategies for Organic Pollutants

Depending on the characteristics and spatial distribution of an organic contaminant in a particular management area there are 3 types of management measures possible: measures that target the source (regional scale), those that target the process (sub-regional scale), or those that target the effects (local scale) (Fig 24).

Source measures aim to isolate or remove the source of contamination, or to reduce the risk of the contaminant source of or multiple contaminants, for example a change in the use of the target chemical or in-situ remediation. This prevents the contaminant to enter the soil system. These are typically measures that are taken at a **local scale**, and could be enforced through legislation. The other two types target the contaminant after they have spread in soil system beyond the scale where source measures are feasible.

Process measures are aimed at the pathway by which the contaminants are transported in the soil system, and are typically performed at a **(sub)regional scale.** These measures can be taken at the start of the pathway. For example, if the contamination has not traveled far yet, for instance through strong retardation than this will have a strong risk reduction effect on for the surface water quality at the end of the pathway. However, if the contaminant is already affecting the quality of the surface water, than measures at the beginning of the pathway, e.g. liming, will take a long time to result in quality improvements for surface water. In these cases, the fastest improvement in surface water quality improvement will result from measures at the end of the pathway, such as vegetated buffer strips.

Effect measures are taken at the contaminant receptor and are typically at the local scale, such as the treatment of groundwater during drink water production.



Range of Management Scales

- Surface water protection (regional scale)
  - Vegetated buffer strips
  - Localized water treatment (run-off, drains)
- Agricultural (pesticide) management (sub-regional scale)
  - Application control (timing, modification of soil conditions, tillage operations)
- Contaminated site remediation (local scale)
  - In-situ remediation
  - Risk-based measures

Fig. 24: Range of scales across the soil-system. Management is focused on the top two, local and regional scales. (Figure adapted from USGS).

4.2.1 Surface water protection (regional scale)

Surface water quality can be controlled by other external sources, outside the region to be managed. These external sources can be, for example an upstream waste-water purification plant, or foreign inflow of cross-border water. However, within a certain region, surface water quality can be also by internal factors of the soil system through surface run-off or groundwater recharge. The relative extent of these factors mainly depends on the regional characteristics, such as topography, and land-use type.

4.2.1.1 Surface run-off

In the case of surface run-off, there are different techniques which could be recommended for mitigation of environmental risk of soil and groundwater pollution on regional scale like:

- Biodegradation (e.g. vegetated buffer strips)
- Immobilization (e.g. Fe/Al oxide-net)
- Photodegradation (e.g. TiO2- and Fe(II)/Fe(III)-systems)

(See chapters 3.1.5.4, 3.1.7 and 3.3.6.11).

4.2.1.2 Groundwater discharge

In the case where groundwater is the main source of surface water contamination, the contaminants are mainly derived from the shallow part of the groundwater, where shorter travel times disallow extensive natural attenuation processes to occur. In contrast, depending on the hydrologic system much of the deeper groundwater can pre-date human influences. As ground and surface water are part of the same hydrologic system the water quality is the result of mixing of groundwater from various depth levels. The upper groundwater is the most polluted by human activities such as farming. The deeper ground water is much cleaner because pollutants substances strongly adsorbed in the shallow subsurface. During dry periods, the surface water fed mainly from the deep, relatively clean groundwater. Under wetter conditions shallow groundwater also contributes to the surface water drainage. After wetter periods the shallow groundwater can flow along very short distances through local drainage systems, such as small ditches, trenches and drains or even through surface run-off (see chapters 3.1.5.1 and 3.3.6.10). Especially with this rapid, shallow transport of contaminants during wet periods results in the loading of contaminants to the surface water system.

Because of differences in chemical properties of the both the contaminants and the soil contaminant penetration depth differs widely. Contaminants that are strongly retarded in soil, only under very wet conditions enter the surface water system. In contrast, more mobile substances penetrate deeper into the groundwater system and can continuously be discharged into the surface water system, even under dry conditions. Pesticide residues which enter the surface water systems by leaching/runoff can be bound to the sediments and can be a source of continuos contamination of water systems (see chapter 3.4.6.10).

Depending on the type of contaminant and soil-system characteristics, different management approaches are available.

The role of physical properties (DNAPL, LNAPL) of the contaminants is also identified as important factor influencing the behaviour of organic contaminants in soils. Since most organic contaminants are non- or only weakly-polar and hydrophobic, they are not miscible with the aqueous phase and are referred as non-aqueous phase liquids (NAPLs). Hydrophobic organic contaminants interact strongly with organic matter and they are also known as oil liking/miscible group (see chapter 3.1.3.1).

With respect to soil-system characteristics there are two main factors:

- The hydrological speed of the soil system, as influenced by:
    - Distance to surface water
    - Thickness of the saturated zone
    - Occurrence of preferential flow
    - Colloid facilitated transport
    - Hydraulic head differences
- The capacity of the soil system to immobilize contaminants is influenced by:

  - Non-ionic sorption processes
  - Ionic sorption processes
  - Biodegradation processes

The effect of the measures for contaminants that are not, or hardly, affected by soil retention processes is mainly determined by the hydrological speed. This means that if input of a particular contaminant is stopped, it will disappear from the soil-system quickly (<10 years). In this case however, as long as the loading of surface water is allowed the effects on surface water will be greatest. If contaminants behavior is significantly controlled by the retention in the soil system then the hydrological speed of the system is less important. In general, the effect of measures is quick when a substance degrades rapidly in the soil system. For example, the biodegradation of glycophosphate, when the substance is still generated and the application can be stopped. Overall however, measures are less effective in the short term when:

- Contaminants are retarded in the soil system through sorption processes
- Previous application of the substances has resulted in accumulation in the soil system.
- There is a slow hydrological system, with thick saturated zones and relatively long average residence times.

4.2.2 Agricultural (pesticide) management (sub-regional scale)

Several risk assessment strategies should be developed for better pollutant management in agriculture (see chapters 3.1.5.4, 3.1.7.1 and 3.3.6.11):

- Monitoring systems in the areas of pesticide application
- Improving management practices in the agricultural field areas to achieve better risk assessment of:
  - Pollutant leaching/run-off
  - Pollutant biodegradation/adsorption

4.2.3 Contaminated site remediation (source removal, local scale)

Management of pollutants in soil should profit from the ability of soil microorganisms to degrade hazardous compounds. The enhancement of pollutant remediation by soil microbes could involve the addition of nutrients, soil condition optimization and the assignment of selected or modified organisms with enhanced degradation capacity. There are three strategies for bioremediation (see chapters 3.1.7.2 and 3.3.6.11). The last two (On- and Off-site) are under more controlled conditions. For all of them the presence of genetically stable microorganisms with good verified degradation capacity for specific pollutant is essential.

4.3 Management Approach: Source→Pathway→Receptor

The risk-based management approach (Fig. 2) allows constructing a risk-based cost-effective approach for the management of contamination in regional areas or mega-sites. It provides a framework to identify major risks, predict future developments and priories measures. The use of natural attenuation options is an integrated part of the risk-based assessment of required measures based on an analysis of contaminant sources, pathways, and receptors.

The risk-based approach for the Rotterdam harbor area considers the combined impact of contamination on the various receptors. These include the surface water systems and the deep groundwater systems below and surrounding the entire port area. The impact is assessed by the current and future plume migration towards these receptors, which is predicted by an extensive fate and transport model. A source-path receptor approach is followed, in which the contaminant sources at the industrial sites form the starting point from which the contaminants will be transported in the direction of the groundwater flow and eventually might reach the receptors. The deep groundwater systems (below and outside the harbor area) and surface water systems are the main receptors at the megasite since, due to the groundwater flow direction, they are in potential danger of receiving contaminated groundwater. In Fig. 25 the major transport pathways of the contaminants to the main receptors are presented.

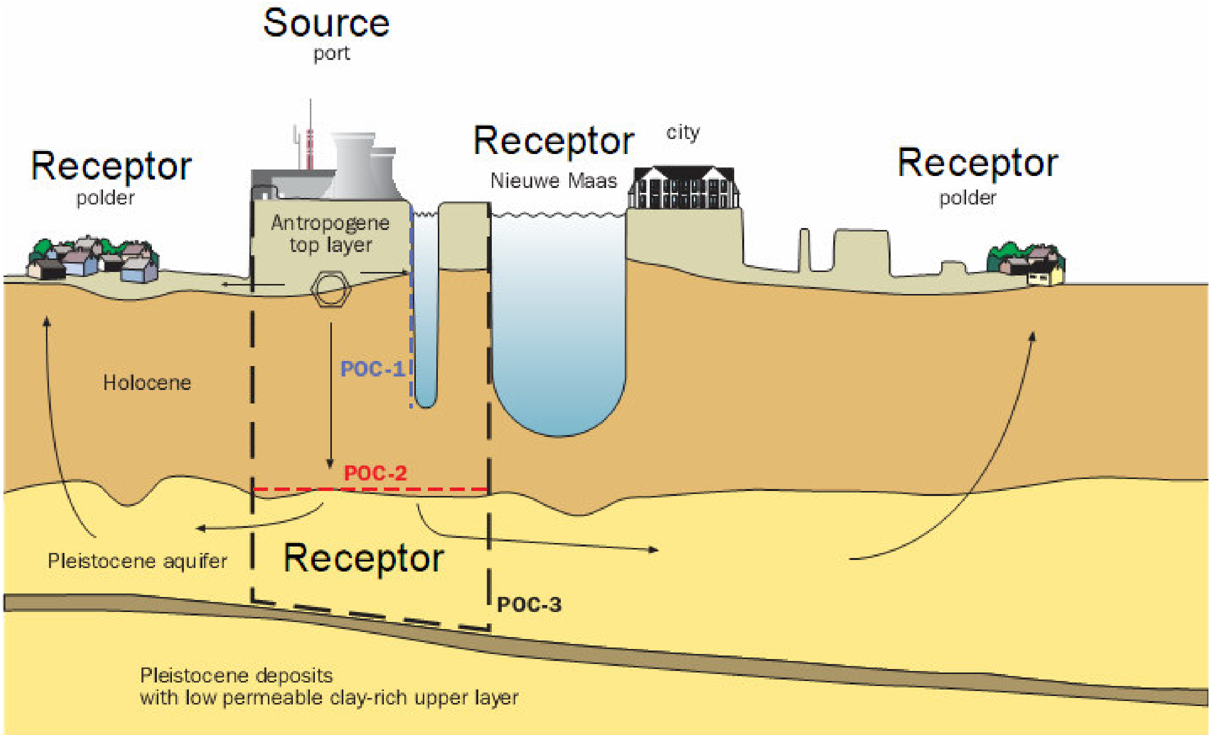


Fig. 25: Example of conceptual model for the risk-based management of contaminants deriving from the Rotterdam Harbor area, using Source-Pathways (arrows) and Receptor approach (Adapted from TNO, 2007).

4.3.1 Degradation in the groundwater zone

In certain soils and under different conditions, there is a risk for groundwater contamination. Degradation potential of organic contaminants is lower in aquifers than in top soil. Soil texture and structure influence the leaching of the organic pollutants to the groundwater. Also, some compound properties (sorption and degradation behavior, volatility), weather conditions (temperature, rainfall distribution) and some other factors (application time and rate, tillage operations) determine the organic contaminant transport to the groundwater zone. Different techniques could be recommended for better pollutant risk mitigation (see chapter 3.1.5.4).

4.4 Framework of Effective Management Measures

It is a well known, that ground contamination is a widespread problem that exhibits a serious threat for groundwater quality. Although, several techniques are available to manage and control contaminated sites, the costs for the evaluation and remediation of contaminated sites often reach such proportions that remediation can not be afforded. Thus, one of the primary approaches to manage contaminants in soils is to profit from their ability to buffer contaminants and to make use of soil microorganisms to degrade these compounds as a possible remediation technique. However, the capacity for natural attenuation of contaminants of soils is still limited and varies from one soil to another. Hence, a better understanding of the fundamental processes in soil and aquifer systems is still needed in order to increase the effectiveness of passive and active remediation techniques. Measures for organic pollutant mitigation could be divided in source, process and receptor measures (Table 6). Different prevention techniques are recommended for better risk assessment (see chapters 3.1.5.4, 3.1.6, 3.1.7 and 3.3.2.11).

Table 6: Types of measures for better risk management.

Types of Measures for Better Risk Management	
Source Measures	• Prevention of release (e.g. leak prevention) • Treatment before release (e.g. at sewage treatment, puridrain) • More efficient application • In-situ remediation
Process Measures	• Improving soil conditions (e.g. stimulate degradation, decrease/increase sorption • Improve hydrological conditions (Increase/decrease residence times or accessibility)
Receptor Measures	• Risk-based management • Protect receptor (e.g. vegetated buffer strips) • Localized treatment at receptor

4.4.1 Source measures

Mitigation strategies for decreasing soil and groundwater pollution through contaminant leaching should focus on pollution risk minimization in the cultivation praxis, and on the improvement of certain soil parameters, which have a decisive role for colloid transport.

A number of mitigation measures in agriculture could be recommended for better mitigation of leaching of the organic contaminants from soil:

- Application restriction for vulnerable soil and/or wet conditions
- Reduction of the application rate
- Adjustment of the application rate to weather conditions
- Use of compounds with higher sorption and/or faster degradation
- Tillage operation which reduce macropore flow and surface run-off
- Collection ponds for tile drain outflow
- Enhancement of In-situ bioremediation

Also, some common measures to reduce surface runoff and erosion from the field such as conservation tillage including zero-tillage, mulching, cover crops, contour plowing/ planting etc, can mitigate pesticide runoff and erosion inputs into surface-waters.

4.4.2 Process measures

Mitigation of the pathways of soil and groundwater pollution can be achieved by improving soil and hydrological conditions to control degradation, sorption and residence times of organic pollutants.
Retention of organic pollutants can be improved due to modification of soil parameters (see chapters 3.1.4.7 and 3.3.6.11):

- pH adjustment
- Improvement of ionic strength (liming or gypsum amendments)
- Incorporation of: organic matter, Fe (in situ oxidation or oxides), low-cost coagulants or biosurfactants

Complete removal of organic pollutants from polluted soil and groundwater sites can be achieved by different remediation techniques. Also, some advanced techniques instead of conventional techniques (e.g. flocculation and sand filtration) (see Chapter 3.1.6):

- Ozonation
- Activated carbon filtration
- Membrane filtration
- Reduction of colloidal dispersibility

Bioremediation is remediation technology which appears to be an efficient, economical and environmental friendly approach (see chapter 3.1.7.1). Different bioremediation measurements can be recommended:

- Adjustment of soil pH conditions
- Better oxygen supply
- Improvement of moisture conditions
- Better nutrient supply
- Implementation of the specialized micro-organisms

For better assessment of soil and groundwater pollution through improved hydrological conditions next measurements can be applied (see chapter 3.1.5.4):

- Reduction of soil surface drying
- Reduction of surface tension
- Claying

4.4.3 Receptor measures

Development of locally precise risk management based on local soil and water characteristics should be implemented in the agricultural management politics. There is a need for development of monitoring systems and improvement of agricultural management practices for better risk assessment (see chapters 3.1.5.4 and 3.3.6.11).

Development of different attenuation strategies can enhance naturally occurring microbial processes without the engineered delivery of nutrients, electron acceptors or other stimulants. Next measurements can be recommended for improvement of utilization of natural attenuation capacity (see chapters 3.1.7.1, 3.1.7.2 and 3.3.6.11):

- The implementation of engineered barrier systems
- Enhancing the natural attenuation by biostimulation or bioaugmentation
- Utilizing the natural attenuation as a stand-alone remedial tool or in combination with other remediation techniques (e.g. Soil vapor extraction, Pump and treat, In situ oxidation and Excavation techniques) mainly in the final cleanup treatment.
- Implementation of the vegetated buffer stripes along the agricultural zones and water bodies to reduce pesticide and fertilization input into surface waters via surface run-off and erosion

4.5 Possibilities to influence the soil/water system

Table 7: Framework of Effective Management Measures

Response to Measure	
Fast Result	**Slow Result**
• Contaminant Factors • Degradable • Changes can be made to current application	• Contaminant Factors • Less degradable, i.e. strong retardation, accumulation in subsoil • Large amounts of application
• Soil Factors • "Healthy" soil ecosystem	• Soil Factors • Disturbed soil ecosystem • Slow hydrological system (long travel times, thickness, hydraulic conductivity) • Poor accessibility (pore size distribution, short-cut flows)

In the Table 7 framework of effective management measures is given. Beside toxicity, biodegradability of organic pollutants can be considered as basic criteria in determining the behavior of xenobiotics in the environment. The knowledge of biodegradability of organic compounds could alter the chemical production to allow environmental risk reduction.

The biodegradability of the man-made chemicals depends on compound structure and degradability by existing microbial enzymes and compound ability to induce or depress the necessary catabolic enzymes production by microbes.
Xenobiotics can affect biodegradability through effects of concentration and chemical structure. Slight modification in molecule structure can make xenobiotics more persistent or more readily biodegradable. The type, number and position of substituent can influence resistance of the organic compounds. Possible changes in the application due to adjustment of the application rates and type of products to the local environmental characteristics could help for better risk assessment.
On the other hand, correction of the soil characteristics through addition of different substances like e.g. organo-clays, organic matter, micronutrients- can change soil and sediment environmental properties.

For more efficient contaminant degradation by soil microbes some measurements can influence the rate of degradation. Nutritional supply of carbon, nitrogen and phosphorus can be recommended for enhancement of biodegradation of xenobiotics in both water and soil environments. Organic carbon content of soil can influence bioavailability due to sorption of different organic compounds. Moisture content in soil influences biodegradation due to water influence on microbes on one hand and on another due to antagonistic relationship with air content in soil pores. Regulation of water content can enhance or depresses biological activities in soil. pH influence chemical transformation if they are acid or base catalyzed. Also, extreme pH conditions in soil affect structure of microbial population. The presence or absence of oxygen has the most important influence on degradation rate and extent of organic pollutant degradation, due to different aerobic and anaerobic degradation pathways.

Bioavailability of organic pollutant depends on sorption to soil solids. As it is already mentioned (see chapters 3.1.4, 3.2, 3.3.2.2 and 3.3.6.4) organic matter and the other soil compounds such as clay or metal oxides can be sorbent for organic pollutants and influence pollutant bioavailability. Sorption of organic pollutants is influenced through combination of soil and pollutant characteristics. There is also a great plant influence on microbes in rhizosphere zone through plant exudates such as carbohydrates, vitamins, amino acids and enzymes.

Glyphosate fate and behavior in soil is affected by different soil factors and processes, but depends also on interaction between the pesticide and soil under the specific local conditions. For glyphosate dissipation ways and time dependent degradation rates is very important influence of soil sorption characteristics, environmental influence, specific soil parameters, behavior of soil microbes and P availability (see chapter 3.3.6).

Better environmental protection of improving management practices of the use and release control of these chemicals could be expected. There is a need for more specified pesticide management based on the adaptation of the pesticide type and application rates to the characteristics of the area of application.

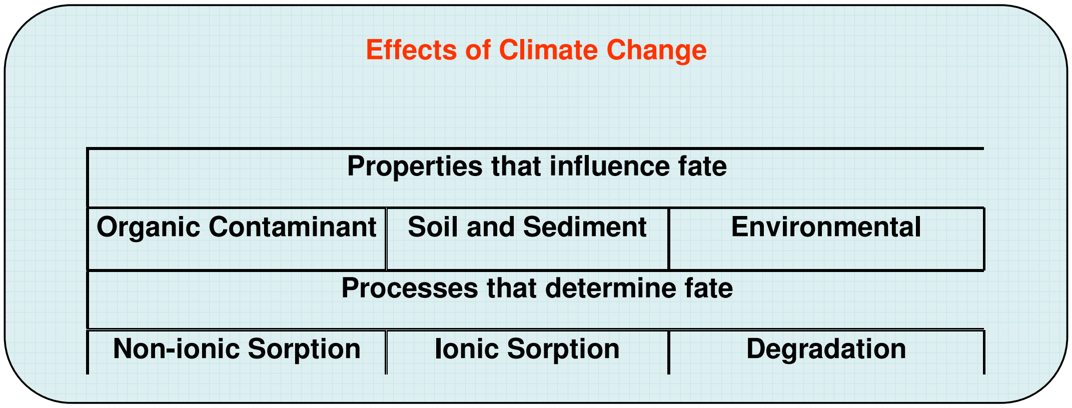
4.6 Effect of climate change on fate organic contaminants

Direct effects of predicted climate changes, like temperature increase, modification of wind and precipitation patterns, sea level rise, snow and ice cover, may influence organic contaminants fate in the environment. Also, future climate scenarios may affect degradation rates of pollutants in the environment, soil properties (and hence land use), air-particle partitioning of chemicals etc (see chapter 3.1.8).

Climate change will affect the following aspects (Table 4):

1. **Environmental** properties
    - Temperature, precipitation
    - biogeochemical changes in: higher activity biomass e.g. organic matter mineralization, affecting DOC concentrations and pH
2. Secondary changes to **Soil and Sediment** properties, due to changes in environmental conditions, e.g. soil cracking under draught conditions, changing redox due to rising water tables. These changes will occur first and foremost in the shallowest parts of the soil.
3. Transport processes
    - Due to physical changes in: water balances, residence times, water tables, water content, soil cracking
4. **Degradation** processes will be likely to be affected first and foremost through indirect effects by climate change.
5. **Inorganic sorption** processes will be affected to a slower and lesser extent

Table 8: Effects of climate change



Effects of Climate Change

Properties that influence fate		
Organic Contaminant	Soil and Sediment	Environmental
Processes that determine fate		
Non-ionic Sorption	Ionic Sorption	Degradation

Prediction of pesticide fate and transport under the future climate changes are very variable and uncertain on one hand. On the other hand, the complexity of the natural environment and different climate-sensitive processes may have conflicting implications for contaminant fate and transport.

The direct impacts of climate change on specific pesticide fate and transport processes will probably have less significant effect on the pollutant fate in environment than land-use changes driven by changes in climate.

Modeling is a powerful approach to obtain a comprehensive understanding of the environmental fate of the pollutants. Spreading of different pollutants in the environment under climate changes could be predicted for better understanding of pollutants behavior under different climatic and environmental scenarios.

5 Realised or planned publication of project results

5.1 Realised publications

- J. Walsch and S. Dultz: Eurosoil 2008 in Vienna – poster „Effects of pH, Ca^{2+}- and SO^{2-} concentration on the surface charge properties of goethite and hematite – Consequences for the adsorption of organic substances“.
- Jochen Walsch: Eurosoil 2008 in Vienna – poster „Effects of pH, Ca^{2+}- and SO^{2-}concentration on the surface charge properties of goethite and hematite – Consequences for the adsorption of organic substances“ (see page 46).
- IOPSIM Poster was presented on the ThinkTank Conference in Amsterdam 2008 and ConSoil conference in Milano 2008.
- The project homepage http://www.wabo.boku.ac.at/iopsim-snowman.html?&L=1 is already active. The next update will be the final version of the results from the accepted final report.
- IfBk: Manuscript for publication in \`Clay Minerals´ with the title: “Effects of pH, Ca- and SO4-concentrations on surface charge and colloidal stability of goethite and hematite - consequences for the fate of organic pollutants” – submitted in January 2009.

5.2 Planed publications

- Manuscript for end-users based on the IOPSIM literature research results, for publication in ITVA-Publication – in preparation.

6 Conclusions/Recommendations/ improvement of project's working area by other organisations noted during execution of the project

This report covers a wide range of issues relevant to the understanding of the mobility of organic contaminants in soil and groundwater systems. The main mechanisms, which are essential for the development of management strategies (immobilization, mobilization and remediation), are relatively well understood. Most results have been derived from controlled laboratory experiments. Nevertheless, in many cases it seems not clear; if or how results from controlled laboratory investigations can be up-scaled and applied to heterogeneous and transient field situations. From these studies it can be concluded that operative mechanisms for any particular interaction between contaminants, soil constituents and soil biota depends on the nature and properties of the soil surfaces, the chemistry of the system (e.g. pH, kind of exchangeable cations, water saturation degree) and the chemical nature of the organic contaminant. In contrast, for the sorption of apolar organic contaminants, the current lack of mechanistic models prevents reliable accurate estimation of retardation effects for a particular contaminant in relation to specific soil characteristics. There is also a lack of information for managing contaminated soils, due to a lack of knowledge about changes in microbial communities.

The limited number of field studies often does not allow defining decisive key processes. Therefore, the management of soil parameters in order to reduce contaminant leaching, to enhance sorption and degradation, is only possible in a general way. Because of the specific properties of each contaminated site there are limitations in generalization of management concepts and strategies. One of the crucial gaps in the prediction and control of contaminant persistence in the environment is the understanding of the mechanisms regulating the bioavailability/biodegradation of pollutants and specifically the limited knowledge about the role of black carbon and soot on biodegradability and sorption processes.

Relevant parameters must be well defined, because otherwise they may cause negative effects on the environment. There is a clear gap of knowledge in fundamental research on models for sorption processes by black carbon and soot, in contrast soil organic matter. There is also a lack of conceptual models for relating contaminant properties with SOM characteristics. Such a model would clearly help to predict sorption behavior. For a better mitigation of pollutant problems, the assessment of soil biodegradation parameters, which control the fate of organic pollutants in soil, should be achieved. Moreover, there is also a lack of knowledge in the assessment of the environmental fate of metabolites.

The results indicate that future research must take also consider multiple management interactions in devising process-based predictions of management effects, including landscape factors. A successful program will require an integrated approach by soil scientists, engineers, chemists and microbiologists. Moreover, there is a need for more detailed information at the molecular level, for a better understanding of the contamination of ground water system. Special research should be dedicated to processes in the sub-soil/ground water system, especially about the microbial degradation in this zone.

Through a locally precise application of pesticide, based on local soil and water characteristics is necessary, the risk of pollution could be considerably reduced. For this, trap systems for different pollutants under different scenarios should be included in future investigation. We also recommend new tests of bioremediation systems, based on the improvement of materials for increasing microbial degradation of organic pollutants under different scenarios. The use of alternative biodegradable additives for a range of pesticide could also reduce environmental risk.

Nowadays, most organic chemicals are measured by specific analytical methods and different procedures are available to assess risks in many cases. However, in order to avoid contamination and related risks, the knowledge of physical, chemical and toxicological properties is of high importance for the handling of chemicals, especially in cases of high production systems. Another need exists for methodological approaches for multi component analysesm in order to measure trace concentrations and the rate of pollutant transformation in different soil and ground water systems.

There is no doubt that even relatively modest climate changes will bring significant environmental impacts. Chemical cycles will be affected in different ways and the interaction between climate change and the possible adaptation/mitigation options that will be used will increase the uncertainties.

The main current problem in applying climate change scenarios for answering those questions is the present lack of understanding of the complex interdependency between climate sensitive processes in the environment and the uncertainties associated with the effects of climate change on economic and social factors.

Seasonal influence on biodegradation (changes in soil temperature, moisture, aerobic conditions) as well as individual and structural microbial response to environmental changes should be investigated in the future projects.

Finally, more intensive investigations are recommended for emerging pollutants, such as veterinary antibiotics or energetic compounds.

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8 Glossary

Glossary of Soil Science Terms 2008

Soil Science Society of America

https://www.soils.org/sssagloss/pdf/soil-science-glossary.pdf

adsorption The process by which atoms, molecules, or ions are taken up from the soil solution or soil atmosphere and retained on the surfaces of solids by chemical or physical binding

adsorption complex Collection of various organic and inorganic substances in soil that are capable of adsorbing ions and molecules.

adsorption isotherm A graph of the quantity of a given chemical species bound to an adsorption complex, at fixed temperature, as a function of the concentration of the species in a solution that is in equilibrium with the complex. Called an isotherm only because adsorption experiments are done at constant temperature.

aerobic (i) Having molecular oxygen as a part of the environment. (ii) Growing only in the presence of molecular oxygen, such as aerobic organisms. (iii) Occurring only in the presence of molecular oxygen (said of chemical or biochemical processes such as aerobic decomposition).

aggregate A group of primary soil particles that cohere to each other more strongly than to other surrounding particles.

aggregate stability A measure of the proportion of the aggregates in a soil that do not easily slake, crumble, or disintegrate.

aggregation The process whereby primary soil particles (sand, silt, clay) are bound together, usually by natural forces and substances derived from root exudates and microbial activity.

anaerobic (i) The absence of molecular oxygen. (ii) Growing in the absence of molecular oxygen (such as anaerobic bacteria). (iii) Occurring in the absence of molecular oxygen (as a biochemical process).

anion An atom or atomic group that is negatively charged because of a gain in electrons.

anion exchange capacity The sum of exchangeable anions that a soil can adsorb. Usually expressed as centimoles, or millimoles, of charge per kilogram of soil (or of other adsorbing material such as clay).

antibiotic An organic substance produced by one organism that in low concentrations will kill or inhibit growth of other organisms.

application rate (i) (irrigation) Rate at which water is applied per unit area; usually in millimeter per hour, (ii) weight or volume of a fertilizer, soil amendment, or pesticide applied per unit area.

aquifer A saturated, permeable geologic unit of sediment or rock that can transmit significant quantities of water under hydraulic gradients.

biodegradable A substance able to be decomposed by biological processes.

biological availability That portion of a chemical compound or element that can be taken up readily by living organisms.

bioremediation The use of biological agents to reclaim soil and water polluted by substances hazardous to the environment or human health.

biostimulation Addition of nutrients to contaminated soil to stimulate indigenous microorganisms to carry out bioremediation.

cation An atom or atomic group that is positively charged because of a loss in electrons.

cation exchange The interchange between a cation in solution and another cation in the boundary layer between the solution and surface of negatively charged material such as clay or organic matter.

cation exchange capacity (CEC) The sum of exchangeable bases plus total soil acidity at a specific pH values usually 7.0 or 8.0. When acidity is expressed as salt extractable acidity, the cation exchange capacity is called the effective cation exchange capacity (ECEC) because this is considered to be the CEC of the exchanger at the native pH value. It is usually expressed in centimoles of charge per kilogram of exchanger ($cmol_c\,kg_{-1}$) or millimoles of charge per kilogram of exchanger.

clay mineral A phyllosilicate mineral or a mineral that imparts plasticity to clay and which harden upon drying or firing.

clayey (i) Texture group consisting of sandy clay, silty clay, and clay soil textures. See also **soil texture**. (ii) Family particle- size class for soils with 35% or more clay and <35% rock fragments in upper subsoil horizons.

coating A layer of a substance completely or partly covering a surface of soil material. Coatings include clay coatings, calcite coatings, gypsum coatings, organic coatings, salt coatings, etc.

colloid A particle, which may be a molecular aggregate, with a diameter of 0.1 to 0.001 µm. Soil clays and soil organic matter are often called soil colloids because they have particle sizes that are within, or approach, colloidal dimensions.

cometabolism Transformation of a substrate by a microorganism without deriving energy, carbon, or nutrients from the substrate. The microorganism can transform the substrate into intermediate degradation products but fails to multiply.

concentration The amount of suspended or dissolved particles or elements in a unit volume or unit mass as specified at a given temperature and pressure.

constant-charge surface A mineral surface carrying a net electrical charge whose magnitude depends only on the structure and chemical composition of the mineral itself. Constant-charge surfaces in soils usually arise from isomorphous substitution in phyllosilicate clay structures.

coulombic forces Those forces caused by electriical attractions and repulsions.

covalent bond The force holding two atoms together that arises from the sharing of electrons.

desorption The migration of adsorbed entities off of the adsorption sites. The inverse of adsorption.

dispersion (i) A term used in relation to solute movement. (ii) The breakdown of soil aggregates into individual component particles.

distribution coefficient (K_d) The distribution of a chemical between soil and water.

drainage Movement of water out of the soil profile.

edge site The edge location on a layer silicate particle that is a source of pH dependent charge.

electrokinetic (zeta) potential The electrical potential at the surface of the shear plane between immobile liquid attached to a charged particle and mobile liquid further from the particle surface.

electron acceptor A compound that accepts electrons during biotic or abiotic chemical reactions and is thereby reduced.

electron donor A compound that donates or supplies electrons during metabolism and is thereby oxidized.

emerging contaminants can be defined as pollutants that are currently not included in routine monitoring programmes at the European level and which may be candidates for future regulation, depending on research on their (eco)toxicity, potential health effects and public perception and on monitoring data regarding their occurrence in the various environmental compartments.

enzyme Any of numerous proteins that are produced in the cells of living organisms and function as catalysts in the chemical processes of those organisms.

equilibrium The state of being physically or chemically balanced, when forces (energy, concentration etc.) equalize such that mass or energy transfer ceases.

erosion (i) The wearing away of the land surface by rain or irrigation water, wind, ice, or other natural or anthropogenic agents that abrade, detach, and remove geologic parent material or soil from one point on the earth's surface and deposit it elsewhere, including such processes as gravitational creep and so-called tillage erosion. (ii) The detachment and movement of soil or rock by water, wind, ice, or gravity

exchangeable anion A negatively charged ion held on or near the surface of a solid particle by a positive surface charge and which may be easily replaced by other negatively charged ions (e.g. with a Cl^- salt).

exchangeable cation A positively charged ion held on or near the surface of a solid particle by a negative surface and which may be replaced by other positively charged ions in the soil solution. Usually expressed in centimoles or millimoles of charge per kilogram.

fertilizer Any organic or inorganic material of natural or synthetic origin (other than liming materials) that is added to a soil to supply one or more plant nutrients essential to the growth of plants.

flocculation The coagulation of colloidal soil particles due to the ions in solution. In most soils, the clays and humic substances remain flocculated due to the presence of doubly and triply charged cations.

flow velocity (of water in soil) The volume of water transported per unit of time and per unit of cross-sectional area normal to the direction of water flow.

fulvic acid The pigmented organic material that remains in solution after removal of humic acid by acidification. It is separated from the fulvic acid fraction by adsorption on a hydrophobic resin at low pH values. See also **soil organic matter.**

groundwater That portion of the water below the surface

of the ground at a pressure equal to or greater than atmospheric.

See also **water table**.

gypsum $CaSO_4 \cdot 2H_2O$. The common name for calcium sulfate, used to supply calcium to ameliorate soils with a high exchangeable sodium fraction.

heterogeneous Media with properties whose variability are not uniform with space.

homogeneous Media with uniform variability with space.

humic acid The dark-colored organic material that can be extracted from soil with dilute alkali and other reagents and that is precipitated by acidification to pH 1 to 2.

humic substances A series of relatively high-molecular weight, yellow to black colored organic substances formed by secondary synthesis reactions in soils. The term is used in a generic sense to describe the colored material or its fractions obtained on the basis of solubility characteristics. These materials are distinctive to soil environments in that they are dissimilar to the biopolymers of microorganisms and higher plants (including lignin). See also **humic acid** and **fulvic acid**.

hydraulic conductivity The proportionality factor in Darcy's law, as applied to viscous flow of water in soil, that represents the ability of soil to conduct water and is equivalent to the flux of water per unit gradient of hydraulic potential.

hydrodynamic dispersion The process wherein the solute concentration in flowing solution changes in response to the interaction of solution movement with the pore geometry of the soil, a behavior with similarity to diffusion

hydrogen bond An intramolecular chemical bond between a hydrogen atom of one molecule and a highly electronegative atom (e.g., O, N) of another molecule.

hydrolysis The chemical reaction that occurs between a substance and water.

hydrophilic Molecules and surfaces that have a strong affinity for water molecules.

hydrophobic Molecules and surfaces that have little or no affinity for water molecules. Hydrophobic substances have more affinity for other hydrophobic substances than for water.

hydrophobic soils Soils that are water repellent, often due to dense fungal mycelial mats or hydrophobic substances vaporized and reprecipitated during fire.

hysteresis A nonunique relationship between two variables, wherein the curves depend on the sequences or starting point used to observe the variables. Examples include the relationships (i) between soil-water content and soil-water matric potential, (ii) between solution concentration and adsorbed quantity of chemical species, and (iii) between soil volume and water content for swelling and shrinking soils.

imbibition Absorption of water into dry soil.

ionic strength A parameter that estimates the interaction between ions in solution. It is calculated as one-half the sum of the products of ionic concentration and the square of ionic charge for all the charged species in a solution. It is needed for calculation of single ion activity.

iron oxides Group name for the oxides and hydroxides of iron. Includes the minerals goethite, hematite, lepidocrocite, ferrihydrite, maghemite, and magnetite. Sometimes referred to as “sesquioxides” or “iron hydrous oxides.”

isoelectric point The activity of potential determining ion in a solution in equilibrium with a variable charge surface whose net electrical charge is zero. For soils it refers to the pH of the isoelectric point of pH-dependent charge materials. It applies only to single components, not mixtures.

K_d See **distribution coefficient, K_d**.

K_{oc} The distribution coefficient, K_d, calculated on the basis of organic carbon content. $K_{oc}=K_d/f_{oc}$ where f_{oc} is the fraction of organic carbon.

K_{ow} The octanol-water partition coefficient. The ratio of the concentration of an organic compound in octanol and in water after equilibration of the two phases.

leaching The removal of soluble materials from one zone in soil to another via water movement in the profile.

loamy (i) Texture group consisting of coarse sandy loam, sandy loam, fine sandy loam, very fine sandy loam, loam, silt loam, silt, clay loam, sandy clay loam, and silty clay loam soil textures. (ii) Family particle-size class for soils with textures finer than very fine sandy loam but <35% clay and <35% rock fragments in upper subsoil horizons.

lysimeter (i) A device for measuring percolation and leaching losses from soil under controlled conditions. (ii) A device for measuring gains (irrigation, precipitation, and condensation) and losses (evapotranspiration) from soil.

macropore Large pores responsible for preferential flow and rapid, far-reaching transport.

macropore flow The tendency for water applied to the soil surface at rates exceeding the upper limit of unsaturated hydraulic conductivity, to move into the soil profile mainly via saturated flow through macropores, thereby bypassing micropores and rapidly transporting any solutes to the lower soil profile. See also **preferential flow**.

microbial biomass (i) The total mass of living microorganisms in a given volume or mass of soil. (ii) The total weight of all microorganisms in a particular environment.

microbial population The sum of living microorganisms in a given volume or mass of soil.

microbiota Microflora and protozoa.

micropore A class of pores that are sufficiently small that water within these pores is considered immobile, but available for plant extraction, and solute transport is by diffusion only (see pore-size classification).

mineral A naturally occurring homogeneous solid, inorganically formed, with a definite chemical composition and an ordered atomic arrangement.

mineralization The conversion of an element from an organic form to an inorganic state as a result of microbial activity.

nutrient Elements or compounds essential as raw materials for organism growth and development.

oxidation The loss of one or more electrons by an ion or molecule.

permanent charge The net negative (or positive) charge of clay particles inherent in the crystal structure of the particle; not affected by changes in pH or by ion-exchange reactions.

pH-dependent charge The portion of the cation or anion exchange capacity that varies with pH.

physical properties (of soils) Those characteristics, processes, or reactions of a soil that are caused by physical forces and that can be described by, or expressed in, physical terms or equations. Examples of physical properties are bulk density, hydraulic conductivity, porosity, pore-size distribution, etc.

point of zero charge (pznc) The pH value of a solution in equilibrium with a variable charge material or mixture of materials whose net charge from all sources is zero (i.e., anion exchange capacity = effective cation exchange capacity). It is often determined for soils that are low in permanent charge minerals and high in oxides and hydrous oxides of Fe and Al.

pollution The presence or introduction of a pollutant into the environment.

porosity The volume of pores in a soil sample (nonsolid volume) divided by the bulk volume of the sample.

preferential flow The process whereby free water and its constituents move by preferred pathways through a porous medium. Also called bypass flow.

residence time The time required for an individual solute ion or molecule to travel through the soil.

retardation The capability of a soil for slowing or retarding the movement of a solute, and is defined for solutes subject to equilibrium reactions with the soil matrix.

riparian Land adjacent to a body of water that is at least periodically influenced by flooding.

runoff That portion of precipitation or irrigation on an area that does not infiltrate, but instead is discharged from the area. That which is lost without entering the soil is called surface runoff. That which enters the soil before reaching a stream channel is called groundwater runoff or seepage flow from ground water. (In soil science, runoff usually refers to the water lost by surface flow; in geology and hydraulics runoff usually includes both surface and subsurface flow.)

soil amendment Any material such as lime, gypsum, sawdust, compost, animal manures, crop residue or synthetic soil conditioners that is worked into the soil or applied on the surface to enhance plant growth or change physical and chemical soil parameters.

soil characteristics Soil properties that can be described or measured by field or laboratory observations, e.g., color, temperature, water content, structure, pH, and exchangeable cations.

soil microbial diversity Expression of the variety of soil microorganisms and activities at the genetic, species, and soil ecosystem levels; measurements based on communities rather than species.

soil solution The aqueous liquid phase of the soil and its solutes.

soil structure The combination or arrangement of primary soil particles into secondary units or peds. The secondary units are characterized on the basis of size, shape, and grade (degree of distinctness).

soil texture The relative proportions of the various soil separates in a soil as described by the classes of soil texture. The textural classes may be modified by the addition of suitable adjectives when rock fragments are present in substantial amounts; for example, "stony silt loam." The sand, loamy sand, and sandy loam are further subdivided on the basis of the proportions of the various sand separates present.

sorption The removal of an ion or molecule from solution by adsorption and absorption . It is often used when the exact nature of the mechanism of removal is not known.

surface area The area of the solid particles in a given quantity of soil or porous medium.

surface tension The amount of energy required to create a new water surface.

surface-charge density The excess of negative or positive charge per unit of surface area of soil or soil mineral.

surfactant A substance that lowers the surface tension of a liquid.

surge irrigation See **irrigation**.

suspension The state in which particles of a solid are mixed with a fluid but are not dissolved.

sustainability Managing soil and crop cultural practices so as not to degrade or impair environmental quality on or off site, and without eventually reducing yield potential as a result of the chosen practice through exhaustion of either onsite resources or nonrenewable inputs.

synergism (i) The nonobligatory association between organisms that is mutually beneficial. Both populations can survive in their natural environment on their own although, when formed, the association offers mutual advantages. (ii) The simultaneous actions of two or more factors that have a greater total effect together than the sum of their individual effects.

tandem mass spectrometry also known as **MS/MS**, involves multiple steps of mass spectometry selection, with some form of fragmentation occurring in between the stages.

tile drain Concrete, ceramic, plastic etc. pipe, or related structure, placed at suitable depths and spacings in the soil or subsoil to enhance and/or accelerate drainage of water from the soil profile.

tillage The mechanical manipulation of the soil profile for any purpose; but in agriculture it is usually restricted to modifying soil conditions and/or managing crop residues and/or weeds and/or incorporating chemicals for crop production.

conventional tillage - Primary and secondary tillage operations normally performed in preparing a

seedbed and/or cultivating for a given crop grown in a given geographical area, usually resulting in <30% cover of crop residues remaining on the surface after completion of the tillage sequence.

conservation tillage - Any tillage sequence, the object of which is to minimize or reduce loss of soil and water; operationally, a tillage or tillage and planting combination that leaves a 30% or greater cover of crop residue on the surface.

contour tillage - Performing the tillage operations and planting on the contour within a given tolerance.

no-tillage (zero tillage) system - A procedure whereby a crop is planted directly into the soil with no primary

or secondary tillage since harvest of the previous crop; usually a special planter is necessary to prepare a narrow, shallow seedbed immediately surrounding the seed being planted. No-till is sometimes practiced in combination with subsoiling to facilitate seeding and early root growth, whereby the surface residue is left virtually undisturbed except for a small slot in the path of the subsoil shank.

topsoil (i) The layer of soil moved in cultivation. Frequently designated as the Ap layer or Ap horizon. See also surface soil. (ii) Presumably fertile soil material used to topdress roadbanks, gardens, and lawns.

toxicity Quality, state, or degree of the harmful effect from alteration of an environmental factor.

transfer The movement of mass at a point in the soil from one region to another region, e.g., solute movement from adsorbed to solution phases or solute movement from a macropore flow region to a micropore flow region.

transport The movement of mass from one point in the soil to another point in the soil.

vadose zone The aerated region of soil above the permanent water table.

Van der Waals forces Binding force which arises from an induced dipole in a normal molecule which induces a dipole in another molecule thus causing an attraction between them.

variable charge A solid surface carrying a net electrical charge which may be positive, negative, or zero, depending on the activity of one or more species of a potential-determining ions in the solution phase contacting the surface. For minerals and other materials common in soils(e.g. soil organic matter, and oxides), the potential-determining ion usually is H+ or OH-, but any ion that forms a complex with the surface may be potential-determining. See also **pH dependent charge**.

vegetated buffer strip an area of land maintained in permanent vegetation that helps to control air, soil, and water qualityand other environmental problems primarily on land that is used for agriculture. Buffer strips trap sediment and enhance filtration of nutrients and pesticides by slowing down runoff that could enter the local water supply.

well A pipe perforated for a prescribed interval (depth increment) in order to equilibrate with the adjoining aquifer for measurement of the depth to the free-water surface, i.e., water table.

xenobiotic A compound foreign to biological systems. Often refers to human-made compounds that are resistant or recalcitrant to biodegradation and/or decomposition.

9 Annex

- IfBk manuscript in preparation to be submitted to `Clay Minerals´

Effects of pH, Ca^{2+}- and SO_4^{2-}-concentration on the surface charge and colloidal stability of goethite and hematite -consequences for sorption of organic substances-

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Summary

The adsorption of inorganic cations and anions on Fe-oxides affects the transport of anionic organic contaminants from soils into aquatic systems. Variations in soil solution chemistry, especially the presence of multivalent Ca^{2+}- and SO_4^{2-} ions affects the surface charge (SC) and as a consequence the adsorption properties of Fe-oxides. Thus, a sophisticated study on the effects of pH, Ca^{2+} and SO_4^{2-} concentration on SC and dispersion properties of synthetic goethite and hematite was conducted.

The mineralogy of the synthesized oxides was verified by X-ray diffraction. The specific surface area (SSA) was found to be 20 $m^2 g^{-1}$ for hematite and 38 $m^2 g^{-1}$ for goethite. SC was measured with a particle-charge detector (PCD 03 pH; Mütek), generating a streaming current. The positive SC was quantified by titration with the anionic polyelectrolyte PES-Na (Sodiumpolyethylensulfonate), and negative SC with the cationic polyelectrolyte Poly-DADMAC (Polydiallyldimethylammonium-chloride). The stability of the equilibrated oxide suspensions was determined in glass test tubes. After 2h settle time at room temperature, 2ml of each suspension were sampled from the surface and the remaining oxide content was determined in an UV-VIS photometer. Experiments were carried out in the pH-range from 3-10 and in presence of NaCl, $CaCl_2$, Na_2SO_4 and $CaSO_4$ electrolyte, at concentrations up to 5 mmol L^{-1}. As polyelectrolyte-cation complexation reactions might result in SC overestimation, the effects of Ca^{2+}- ions on the adsorption of PES-Na on the oxides were studied with batch adsorption experiments.

Maximum values of positive SC and colloidal stability of goethite and hematite were observed in strongly acidic conditions. Rapid flocculation was observed close to the point of zero charge (pzc), i.e. the point where the streaming potential is zero. A further increase in pH leads to the development of negative SC and stronger repulsive forces which favour dispersion. In presence of Na_2SO_4, SC and colloidal stability was found to decrease with increasing Na_2SO_4 concentration. At pH 4, the addition of 0.1 mmol L^{-1} $Na_2SO_4^{2-}$ induced a decrease in SC from 1500 to 380 $\mu mol_c\ m^{-2}$ for goethite and from 850 to 420 $\mu mol_c\ m^{-2}$ for hematite. Above a Na_2SO_4 concentration of 0.5 mmol L^{-1} and pH >5, the SC of both oxides was found to be always negative. In presence of Ca^{2+} ions, SC quantification of positively charged colloids by titration with PES-Na leads to an overestimation, because of a PES-Ca^{2+} complexation reaction, which decreases the negative charge of the polyelectrolyte. From batch experiments it was observed that the adsorption of anionic PES-Na polyelectrolyte is significantly enhanced in presence of divalent Ca-cations, which can be attributed to (1) complexation, resulting in reduced charge of the PES-Na polyelctrolyte, (2) formation of cation bridges between negatively charged groups of the oxides and the polyelectrolyte, and (3) higher ionic strength, that increases the thickness of the adsorbed layer.

Overall it can be concluded, that sorption of anionic organic substances might be diminished in presence of SO_4^{2-}, either due to competitive effects or due to a reduced positive SC of the Fe-oxides. In contrast, the presence of divalent cations might enhance the adsorption of organic ligands, even at higher pH. For predicting the fate of organic contaminants it is important to consider soil solution chemistry.