

Proceedings of the 2nd International Workshop on Integrated Soil and Water Protection: Risks from Diffuse Pollution (SOWA)

held in Prague, Czech Republic, from 28 to 29 June 2004

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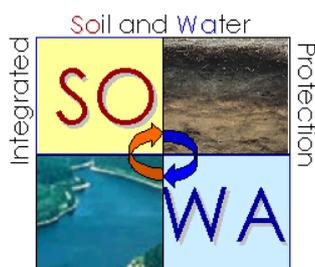
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Foreword

Dear Workshop-Participant,

we welcome you in Prague to the 2nd International Workshop on Integrated Soil and Water Protection: Risks from Diffuse Pollution (SOWA).

Soil pollution and degradation is a result of population growth and technological development. Industrial development has brought prosperity to millions of people, but has also left a legacy of environmental damage that continues to impact natural resources and ultimately the human well being. A wide range of man-made chemicals designed for use in industry, agriculture, pest control, consumer goods, and emissions from the combustion of fossil fuels are the main sources for diffuse pollution. Within the water cycle, soils act as the key zone for storage, filtration and transport of water and associated pollutants. If the accumulation of pollutants exceeds the buffer capacity, then soils or sediments can become the source of diffuse pollution of adjacent compartments such as for groundwater and surface waters.

In the EU Soil Thematic Strategy (DG ENV - *Towards a Thematic Strategy for Soil Protection*, COM(2002), 179 final), diffuse pollution is itemised as main threat to the soil by direct or either indirect pollution due to the disposal/use of sewage sludge, incineration sludge, compost and pesticides.

The leitmotif of this workshop is to focus on the risks arising from the continuous pressure of man onto soils leading to damage of crucial soil functions such as:

- Base for ecosystem quality, sustainable land use and safe food production
- Filter for drinking water
- Key compartment in global biogeochemical cycles (carbon, nitrogen, water...)
- Sink/source for anthropogenic and natural pollutants

The most relevant scientific questions for future research such as the physico-chemical multifunctionality of soils, long-term vs. short term issues and European/global scale opposed to local dimensions will be discussed. Leading scientists are invited to address the key topics of the workshop.

We wish you a fruitful workshop with moved discussions on these different topics of diffuse pollution. In addition, we wish you a pleasant stay in Prague during the workshop and hopefully, you will have enough time to discover the wonderful and inspiring ambience of the city of Prague – within the heart of Europe.

Tübingen, June 2004

Dietrich Halm, Peter Grathwohl

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The workshop organisers are grateful to all who assisted in preparing this conference. Especially, they would like to thank the members of the Scientific Committee and the six invited key note speakers who brought new and specific input to the workshop.

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**SESSION I:
INVENTORY: IDENTIFICATION OF PRIORITY
COMPOUND CLASSES**

KEY NOTE: Organic pollutants in sewage sludges: from detergent-derived chemicals to human-use antibiotics

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1 Introduction

Sewage sludge has been disposed on agricultural land over a long time. This utilization of sewage sludge has been subject to provisions in several countries and in particular in the European Union, which has quite recently developed a draft of a “*Working document on sludge*” (EU 2000), to promote the use of sewage sludge in agriculture while improving the safety and harmonize quality standards. It proposes limit values for concentrations of heavy metals and organic compounds that should restrict the use of sewage sludge in agriculture if the limits are exceeded. The third draft of the “*Working document on sludge*” proposes limit values for concentrations of the following organic compounds or compound groups if sludge is to be used in agriculture:

- A. Polychlorinated biphenyls (PCBs)
- B. Polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD, PCDFs)
- C. Sum of halogenated organic compounds (AOX)
- D. Polycyclic aromatic hydrocarbons (PAHs)
- E. Di(2-ethylhexyl)phthalate (DEHP)
- F. Linear alkylbenzenesulfonates (LAS)
- G. Nonylphenol and nonylphenolethoxylates with 1 or 2 ethoxy groups (NPE)

The contaminants A to D are persistent organic pollutants (POPs), which are widely distributed in the many parts of the environment. Since May 2004 the POPs are regulated by the Stockholm POP convention. The plasticizer DEHP is also entering the environment from many sources. However, LAS and NPE are typical sewage-borne pollutants.

The report on “*Organic Contaminants in Sewage Sludge for Agricultural Use*” (Langenkamp et al., 2001) aimed at providing an overview on the (a) occurrence of organic compounds in sewage sludge, (b) basic toxicological data, (c) on the persistence of organic contaminants in soils, (d) on the risk assessment for the various pathways and (e) possibly a priority list of organic contaminants. This study also attempted to summarize conclusions of the pertinent publications and to point out where further information is needed.

The purpose of this presentation is to review the knowledge on detergent-derived contaminants in sewage sludges and to report on the occurrence of several so-called emerging contaminants. The latter substances or substance groups might also be included in a candidate list of sludge contaminants, for which a risk assessment should be performed with regard to the use of sewage sludges on agricultural soils. Special emphasis will be put on polybrominated flame retardants, musk fragrances and on human-use antibacterials, which are all known to occur in municipal wastewaters. Based on their position in a polarity-volatility, the various contaminants can be evaluated regarding their potential for accumulation in sewage sludges.

2 Detergent-derived chemicals

Detergents are used in large quantities for laundry and cleaning of surfaces in households, in institutions and in industry. These chemicals are used together with water and are subsequently discharged into industrial and municipal wastewaters. During wastewater treatment the detergent

ingredients are either biodegraded or eliminated through sorption onto sewage sludge. Consequently, sewage sludges contain several groups of detergent-derived contaminants. The following list encompasses those detergent-derived sludge contaminants, on which elaborated studies have been performed.

- A. Amphiphilic anionic surfactants such as linear alkylbenzenesulfonates (LAS) or secondary alkylsulfonates (SAS).
Brunner et al. 1988; Giger et al. 1989, Marcomini et al. 1989; Field et al. 1994; Riu 2001.
- B. Lipophilic metabolites of nonionic surfactants such as nonylphenol (NP).
Giger et al. 1984; Ahel et al. 1994; Marcomini et al. 1989; Pryor et al. 2002; Lee et al. 2004.
- C. Cationic surfactants ditallowdimethylammonium cation (DTDMAC).
Fernandez et al., 1996.
- D. Fluorescent whitening agents. Poiger et al. 1993, 1998.
- E. Musk fragrances. Kupper et al. 2004; Herren and Berset 2000.

An overview will be presented on the concentrations of these pollutants in sewage sludges with a particular emphasis on residual levels in anaerobically digested sludges. It becomes evident from Fig. 1 that the type of sludge stabilization (anaerobic or aerobic) has a significant impact on the residual levels of NP and LAS in the sewage sludges. In the case of nonylphenol, the sludge contents are also discussed in relation to changed inputs over the last 20 years (see Fig. 2). The nonylphenol levels in the digested sludges reflect several measures for reducing the use of nonylpolyethoxylate surfactants such as the Swiss ordinance on environmental pollutants (1986) and voluntary reductions by the manufacturing companies.

Nonylphenol und LAS in sewage sludge

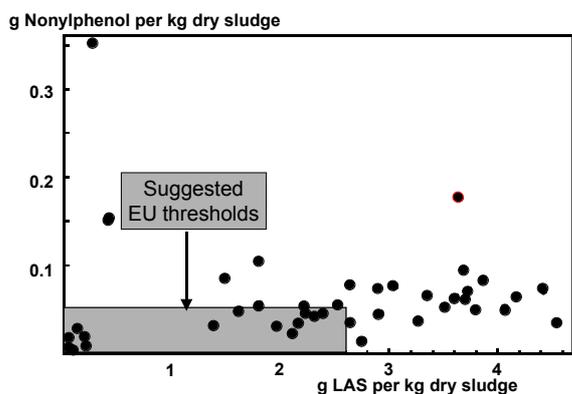


Figure 1
Concentrations in anaerobically and aerobically stabilized sewage sludges in Switzerland. LAS: linear alkylbenzenesulfonates, very widely applied anionic surfactants. NP: nonylphenol, a metabolite of nonylphenol-polyethoxylates used as nonionic surfactants.

Nonylphenol in digested sewage sludge

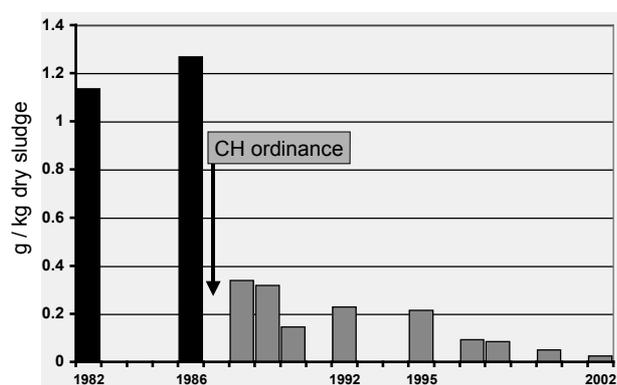


Figure 2
Concentrations of nonylphenol in digested sewage sludges in Switzerland from 1982 to 2002. In 1986 the Swiss ordinance on environmental pollutants banned the use of nonylphenol-polyethoxylate surfactants in household laundry detergents.

3 Musk fragrances

Several nitro and polycyclic musk fragrances were quantified in sewage sludges: Musk ketone and musk xylene were the most abundant substances predominantly in municipal sewage (low $\mu\text{g}/\text{kg}$ dry matter). The major polycyclic musks were galaxolide and tonalide (Herren and Berset 2000; Kupper et al. 2004). In addition, amino metabolites were detected. Mean values in stabilised sludge from 16 Swiss wastewater treatment plants were 20.3 mg/kg d.w. for galaxolide, 7.3 mg/kg d.w. for tonalide and 1.8 mg/kg d.w. for the galaxolide–lactone. Contents of celestolide, phantolide and traseolide were between 0.1 and 1.8 g/kg d.w. (Kupper et al. 2004). These results show that polycyclic musks origin

mainly from private households and that loads from craft industry, industry and atmospheric deposition are negligible. The technology of wastewater treatment and sludge processing seems to be of minor importance for degradation processes of polycyclic musks. The calculated input in wastewater of polycyclic musks is lower by a factor of 5–7 than the estimates based on use volumes. Degradation processes, other emission pathways than wastewater or inappropriate estimation of production volumes, might explain this discrepancy.

4 Polybrominated flame retardants

Brominated flame retardants are ubiquitously occurring persistent organic pollutants. In particular the polybrominated diphenyl ethers (PBDE) but also the tetrabromobisphenol A (TBBPA) and hexabromocyclohexane (HBCD) are considered new POPs which can also be detected in municipal sewage sludges (e.g. Hale et al. 2001, 2003; Metzger and Kuch 2003; Kohler et al. 2003; Hites 2004).

Mean concentrations observed in German sewage sludges were approximately 100 µg/kg d.w. for the sum of tetra- to heptabromodiphenyl ethers and 16 µg/kg d.w. for TBBPA (Metzger and Kuch 2003). Possible pathways how these flame retardants enter wastewater are most likely textiles and in some cases process waters from the production of flame retardants itself. Since significant amounts of TBBPA (up to 25 µg/kg d.w.) and PBDE (up to 180 µg/kg d.w.) in toilet paper, this may also be a pathway. Recycled toilet paper contained significantly higher concentrations than not recycled paper. Possibly this contamination could come from the ink used for printing or special flame-protected papers used for recycling; obviously, the de-inking process does not remove these compounds from the paper.

Kohler and co-worker (2003) found about five times increased average concentrations of decabromodiphenyl ether in Swiss sewage sludges of 2002 compared to sludges of 1993 (from 0.22 to 1.1 mg/kg d.w. In the same sludges pentabromodiphenyl ether decreased to 50%. Substantially higher levels of penta- and decabromodiphenyl ethers (1.5-1.5 and 0.4-1.0 mg/kg d.w.) were found in Wisconsin and in a survey in the U.S.A. compared to the analogous European values (Hale et al. 2003).

5 Antibiotics

Environmental analytical studies show that trace concentrations of antibacterial agents (antibiotics) and other pharmaceuticals occur in hospital and municipal wastewaters and in the aquatic environment. Fluoroquinolones (FQs), sulfonamides and macrolides are three important human-use antibiotic classes, which were studied in detail (Giger et al. 2003, Golet et al. 2002, 2003). The most abundant FQs ciprofloxacin and norfloxacin are substantially eliminated in wastewater treatment (80–90%) by sorption transfer to sewage sludge (see Fig. 3). The FQs occur at concentrations from 1.4 to 2.0 and from 2.1 to 2.4 mg/kg d.w. in raw and digested sewage sludges, respectively (see Fig. 4., Golet et al. 2003b). Field experiments of sludge-application to agricultural land confirmed the long-term persistence of trace amounts of FQs in sludge-treated soils and indicated a limited mobility of FQs into the subsoil. Sludge concentrations of sulfonamide and macrolide antibacterials ranged from below 0.015 to 0.25 mg/kg d.w. reflecting the much lower elimination of these chemicals by sludge sorption in wastewater treatment (Göbel, Ph. D. thesis 2004).

Mass fluxes of ciprofloxacin in wastewater treatment

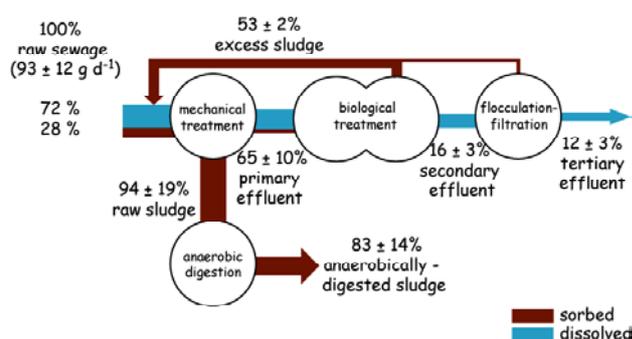


Figure 3:
Results of mass flow analyses for the FQ antibiotic ciprofloxacin in wastewater treatment (Golet 2003)

Fluoroquinolones in sewage sludge

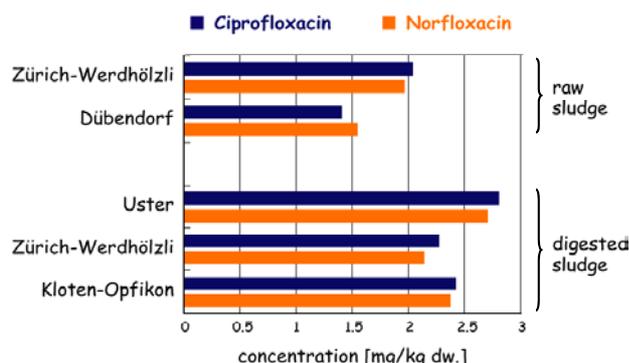


Figure 4:
Sludge concentrations of ciprofloxacin and norfloxacin (Golet 2002, 2003)

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Profiles of PAHs in contaminated soils from industry regions (Poland)

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Abstract: The present paper describes an attempt to do a correlation between profiles of 16 PAHs occurring in soils depending on their origin. To reach this goal, samples of topsoils were examined. These samples were taken between 0-100 cm depth and in some cases, samples of soils drawn on top of the groundwater level were taken. Determinations of PAHs were performed in samples collected from industrial sites (cooking plant, benzol processing plant, and oxo-synthesis processing). On the other hand, the obtained results were compared with PAH-concentrations in samples from forest and agricultural areas. Profiles of PAHs in soils were compared with profiles of these compounds occurring in organic pollutants which were emitted by combustion of solid fuels and from cooking processes.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are extremely harmful to the natural environment. These compounds are emitted into the environment from combustion processes of solid and liquid fuels, by metallurgy, transport and cooking processes. PAHs, including benzo(a)pyrene, are characterised by a high muta-, terato- and carcinogenic activity. The determination of these compounds becomes a very important element of environmental monitoring. In the case of industrial soils, there are more than two ways of impact of the PAHs to the environment: non-safety waste deposits, air deposits and wastewater leakages. Persistent PAHs tend to accumulate in environmental compartments such as soils.

2. Materials and Methods

2.1 Sampling

Soil samples were collected from depths of 1 m (layer 1) and from the top of the groundwater level (layer 2). In the some cases, samples were taken from the medium layers. The sampling points were located in industry areas (cooking plant, benzol processing plant, oxo-synthesis) and agricultural areas.

2.2 Analytical Methods

The concentration of PAHs was determined by the following methodologies: ultrasonic field extraction and separation of aromatic fraction. The aromatic fraction was qualitatively and quantitatively analysed by means of the gas chromatography coupled with the mass spectrometry. The methodology is described in Czaplicka et al (2002).

3. Result and Discussion

The investigations showed an occurrence of PAHs in all samples. The concentration levels of PAHs depended on the way of the area exploitation. PAH concentrations in a topsoil amounted up to 280 mg/kg. This concentration level indicated the discordance to Polish National Standard for soils. The higher PAH content was observed for topsoils from a closed cooking plant. Comparisons obtained for layer 1 and 2 of the same sampling point showed a considerable differentiation in the PAH content. Soils from the top of the groundwater level showed PAHs concentrations which are in accordance with the Polish law. Fig. 1 present PAH contents in soils from a cooking plant and industry areas.

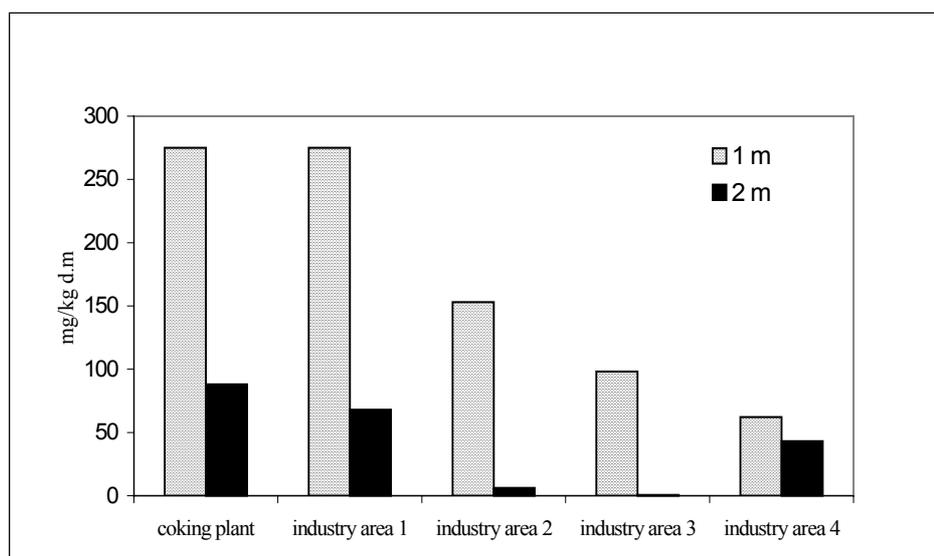


Figure 1: PAH contents in soils

Table 1: PAH contents in soils of an oxo-synthesis plant

Compound	Depth, m		
	0,5	1,5	2,2
Naphthalene	5,467	no	no
Phenanthrene	2,073	22,268	0,180
Anthracene	1,362	11,470	0,083
Fluoranthene	3,296	44,255	0,382
Chrysene	0,431	54,515	no
Benzo(a)anthracene	6,058	43,150	no
Benzo(a)pyrene	0,001	5,671	no
Benzo(a)fluoranthene	0,001	1,222	no
Benzo(g,h,i)perylene	no	0,347	no
Total PAHs	18,689	182,898	0,645

In addition, some anomalies were observed. In the samples of an oxo-synthesis plant (1,5-2 m depth), higher PAH concentrations were observed in compared to samples from topsoils and the top of the groundwater level (Tab. 1). This phenomenon was probably a result of a long lasting industrial exploitation and surface transformation during the building work. We suppose that in this place, probably a local waste magazine was located, which was filled during the building works. This conclusion is confirmed by the PAHs profiles.

In the case of agriculture samples, the discordance to Polish National Standard was observed too. It was probably a result from the influence of air deposits. The sampling point was localised in the neighbourhood of the industrial area and a speedway. Additionally, in this place the winds blow mainly from tze direction of the cooking plant. The PAH profiles (Fig. 2) are very similar to the PAH profiles, which were adsorbed from air (Czaplicka et al 2002, Klejnowski et al. 2002). We suppose that in this case dust deposits are the major source of pollutants.

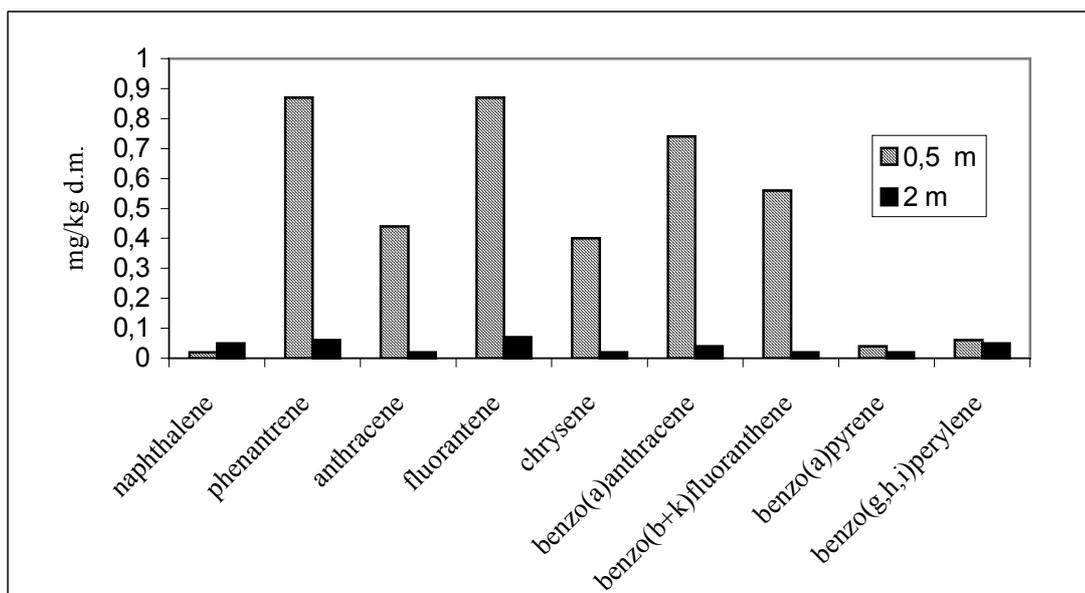


Figure 2: Profile of PAHs in agriculture soil

PAHs profile in sample from cooking plant (Fig. 3) correspond with PAHs profile in cooking tar. In the case of topsoil the characteristic ratio of phenanthrene to anthracene (3:1) was observed.

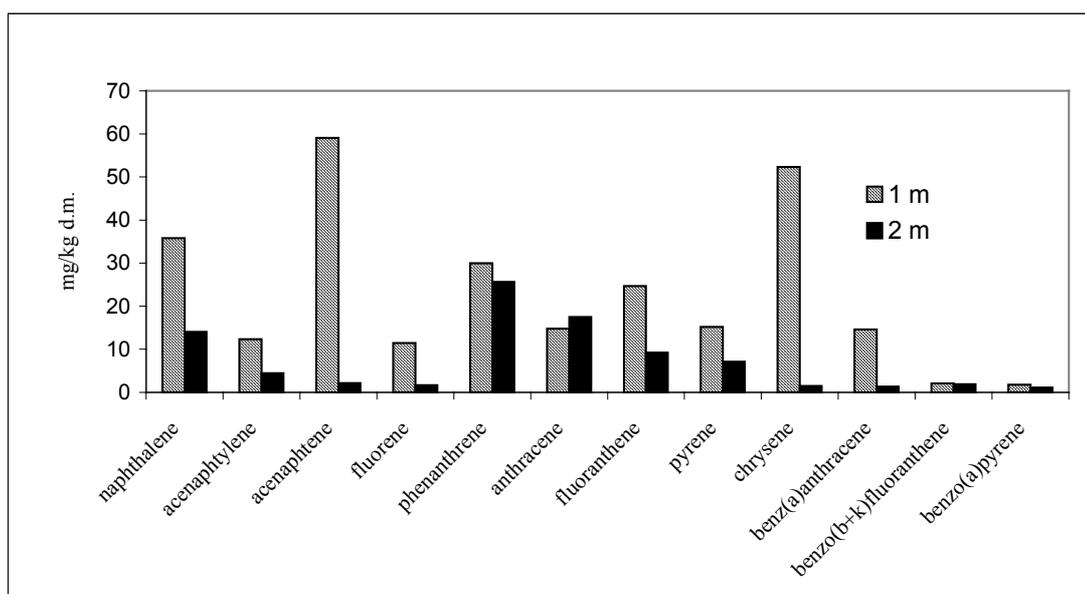


Figure 3: PAH profiles of a topsoil from a cooking plant

4. References

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Contaminants in arable soils fertilised with sewage sludge

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Abstract: The aim of this study was to establish if the entry of contaminants into the soil through the application of sewage sludge may lead to a demonstrable increase in their levels in the soil. The main outcome of this study has been a demonstration of an accumulation of contaminants in the soil at 3 out of 11 agricultural field locations and 2 experimental study locations as a consequence of many years of application of sewage sludge. Higher concentrations of organotin compounds and polycyclic musks, as well as copper and zinc, were found at the 2 field locations to which the highest quantities of sewage sludge had been applied. The concentrations of organotin compounds and dioxins (PCDD/PCDF) were significantly elevated at one further agricultural field location. The experimental study locations were found to have higher levels of the above substances and, in addition, of cadmium, lead and mercury, as well as PCBs, PAH and DDT. A further point is the apparent high persistence of the organic compounds in the soil over a relatively long period of time since the last sludge application – up to 14 years. The heavy metal concentrations at the experimental study locations lay both above and below the precautionary values laid down in German Soil Protection Ordinance (Bundes-Bodenschutz- und Altlastenverordnung, BBodSchV). The values for the agricultural field locations were below the precautionary values.

1. Rationale for the study

One focus of current discussions in Germany on the application of sewage sludge to soil, and the forthcoming amendment of the corresponding legislation (Klärschlammverordnung AbfKlärV), is the anticipated long-term accumulation of contaminants in agricultural soils. The presence in the soil of a large number of organic substances that give cause for concern in terms of toxicology, and that are not covered by the German sewage sludge legislation, gives rise to unquantifiable risks. The resolutions adopted at the joint conference of Agriculture and Environment ministers in June 2001 were intended to avoid any increase in the concentrations of contaminants in the soil as a result of agricultural activities. The presence of a wide range of organic contaminants in sewage sludge has been demonstrated in recent studies, including studies carried out in the German states of Baden-Württemberg and Nordrhein- Westfalen. However, there is insufficient data available on their fate in arable land to which sewage sludge has been applied.

2. Study Concept

The study was based on a comparison of pairs of fields, one of which had sewage sludge applied to it (sewage sludge field) and the other a reference field without sewage sludge application (reference field).

Locations

The study locations were selected on the basis of the following criteria to enable an attribution of increased substance concentrations present in the soil to the application of sewage sludge:

I The reference field without sewage sludge application was selected close to the sludge field and had soil and site characteristics that largely correspond to the sludge field. **II** The soils in the sewage sludge fields have had many years of recorded application of, as far as possible, high quantities of sludge within the statutory limits. **III** The sewage sludge fields should be largely uninfluenced by the usage of farmyard manure (especially liquid manure). **IV** The 11 agricultural field locations were distributed over different agricultural regions of Baden- Württemberg. The selection resulted in 13 study locations distributed over Baden-Württemberg, each comprising a sewage sludge field and a

reference field. There were a total of 11 agricultural field locations (Nos. 3 to 13), as well as 2 experimental locations (Nos. 1 and 2) on the campus area of the University of Hohenheim (2 plots of a former sewage sludge high-load study). The quantities of sewage sludge applied to the agricultural sewage sludge fields lay between 3.2 t/ha and 31.5 t/ha in total. The corresponding values for the experimental sewage sludge field plots were 85 and 510 t/ha (the reference field here corresponded to the zero plot). The selection of locations thus yielded only a few agricultural field locations that had high sewage sludge application over several years. Nevertheless, increases in the concentrations of various substances as a result of the application of sewage sludge were evident.

Substance groups investigated

The selection of the substance groups was based, inter alia, on a substance list elaborated by the UMK-AG (working group on behalf of the conference of Environment Ministers) titled “Reasons for the Presence of Hazardous Substances in Sewage Sludge and Action Plan” (UMK-AG, 2000). Measurements were carried out for heavy metals (and As and Sb), and for organic substance groups of “high relevance” and substances for which “more information is required”, as stated in the UMK-AG (Table 1). Analysis of heavy metals was conducted using 3 parallel samples and 3 different extraction methods (aqua regia, EDTA and ammonium nitrate solution). The analysis of organic compounds (except for PAH, PCBs and CHC) was initially confined to selected locations and single samples for cost reasons. Where locations were found to have higher substance concentrations, a total of 3 parallel samples were taken and subjected to statistical analysis.

3. Results

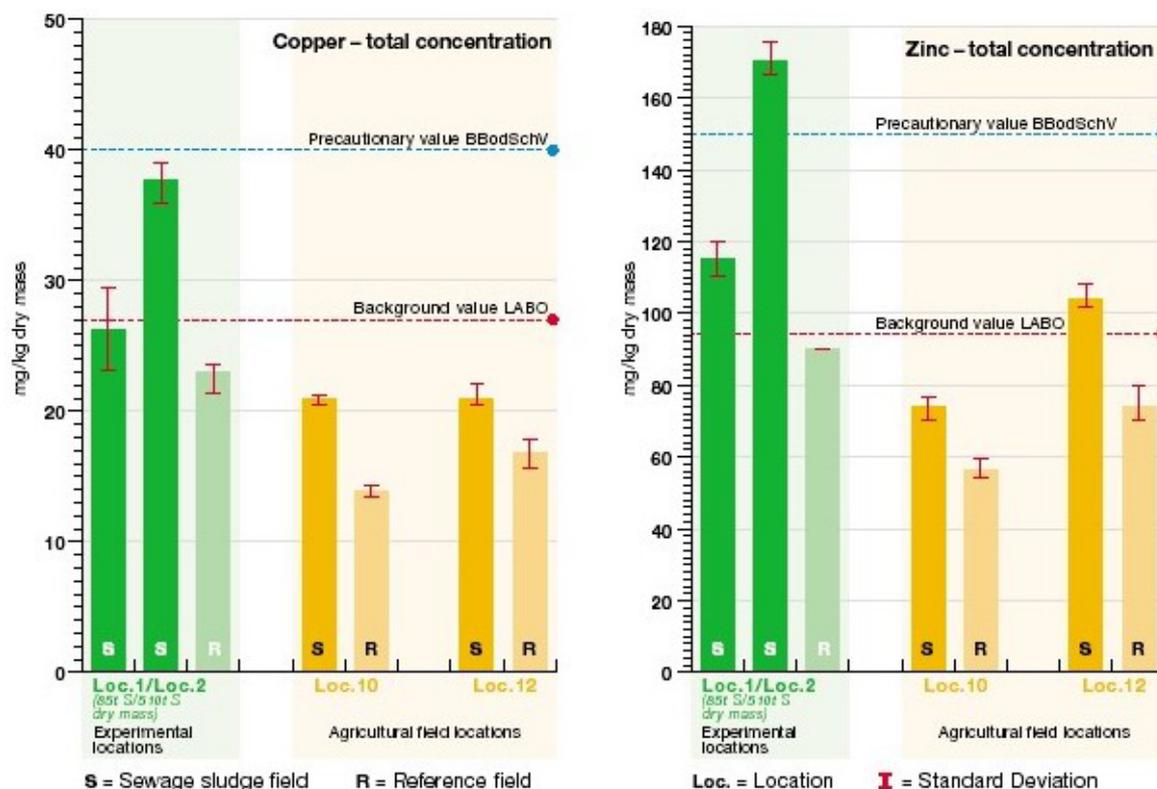
3.1 Heavy metals

The total heavy metal concentration (extracted with aqua regia) for 3 out of the 11 agricultural field locations was significantly elevated on the sewage sludge field for at least 1 heavy metal (see Table 2 and Figures 2 and 3). At locations 10 and 12 the values were significantly higher for 4/2 heavy metals on the sewage sludge fields and yielded a clearly increased incidence of elevated concentrations. These 2 locations were those that had received the highest quantities of sewage sludge (31.5 and 19 t/ha respectively). With regard to the variety of analysed heavy metals (aqua regia extract), the values obtained for Cr (1), Cu (3), V (1) and Zinc (2) were conspicuous. Extraction with EDTA again yielded significantly higher concentrations for heavy metals from the sewage sludge fields – Nos. 10 (Zn) and 12 (Cu and Zn). Extraction with ammonium nitrate did not yield any relevant results, at least for the agricultural field locations. The results for the experimental locations (Nos. 1 and 2)

Table 1: Overview of the substances investigated

Heavy metals
As, Cd, Co, Cr, Cu, Mo, Ni, Pb, Sb, Ti, Hg, V, Zn
Organic substances
- Polycyclic aromatic hydrocarbons (PAH)
- Polychlorinated biphenyls (PCBs)
- Organochloropesticides (CHCs - 3 substance groups)
- Dioxins / furans (PCDD/PCDF)
- Octyl-/Nonylphenol (AP)
- Polycyclic musks
- Phthalates (DEHP)
- Polybrominated diphenylethers (PBDE)
- Organotin compounds (OT)
- Linear alkylbenzene sulfonates (LAS)
- Bisphenol A
- (Medicinal products, investigated at one location only and not found)

also revealed a clear relationship between the quantities of sewage sludge applied and the heavy metal concentrations. The value for Hg at location 1 (85 t/ha sewage sludge) is significantly higher. At location 2 (510 t/ha sewage sludge) the values for 7 heavy metals (Cd, Cu, Mo, Pb, Sb, Hg, Zn) were significantly higher than for the reference field (zero plot). The heavy metals Ni and Zn soluble in ammonium nitrate were significantly elevated for location 2. In addition to possible differences in contaminant concentrations between sewage sludge fields and reference fields, the concentrations of heavy metals were also compared to the background and precautionary values given in the federal soil protection ordinance (BBodSchV). The values found at locations 1 and 2 exceeded the precautionary values for the elements Cd, Hg and Zn, and also exceeded the background values for Cu and Zn (Fig. 2/3). The value for Zn (ammonium nitrate extraction) at location 2 almost approaches the examination value for adverse affects on the growth of cultivated plants. All of the values found for the agricultural field locations were below the precautionary values given in BBodSchV.



Figures 2/3: Total copper concentrations (Fig. 2) and total zinc concentrations (Fig. 3) for selected locations compared to the background value given by the LABO (1998) and the BBodSchV precautionary value.

3.2 Organic contaminants

Significant differences were found between the sewage sludge fields and reference fields at 3 out of the 11 agricultural field locations (Nos.10, 12 and 13) for at least 1 organic parameter. The concentrations of polychlorinated dioxins/furans, the organotin compounds and the polycyclic musks were significantly elevated at 3 locations (Figs. 4 - 6). At locations 1 and 2 the values for all organic parameters with concentrations above the specified limits of quantitation (8 out of 13 organic substance groups investigated) were significantly higher for the sewage sludge fields than the reference field. The differences were smaller at location 1 since less sewage sludge was applied there. The inclusion of these experimental locations in the study has provided useful information since the high sewage sludge quantities provides data on the effects of long-term contaminant entry through application of sludge. In addition, the typical non-ubiquitous organic contaminant pattern of soils fertilised with sewage sludge was established, with the analytical limits of quantitation very clearly exceeded in some cases. Representatives of these substance groups (e.g., polycyclic musks) were still present in the soil even though the last experimental application of sludge was in 1989 (14 years ago).

4 Conclusions

Evaluation of the overall results showed a causal relationship between the application of sewage sludge and the increased concentrations of contaminants on the experimental locations 1 and 2 and the agricultural field locations 10, 12 and 13. The values were significantly elevated for Cu, Zn, PCDD, polycyclic musks and organotin compounds at the fields to which sludge had been applied. These conclusions are supported by the following observations/arguments:

- The differences in the analytical results between sludge and reference fields were statistically significant.

- Alternative routes of entry – such as the entry of heavy metals or PCDD/PCDF through atmospheric deposition or liquid manure – and landscape/geological causes can be ruled out because of the close proximity of the sewage sludge and the corresponding reference field and their similarity in terms of soil properties.
- There was a clearly increased incidence of higher values for the samples from agricultural field locations 10 and 12 to which the highest quantities of sludge were applied, as well as a good correlation, in part, with the substance spectrum of the experimental locations 1 and 2 that had received very high quantities of sludge.
- The spectrum of organic compounds found on the sewage sludge fields is typical for sewage sludge and is in agreement with the results already obtained for sludge investigations. The concentrations of polycyclic musks are of particular interest as their pattern of usage means that their only relevant route of entry is through sewage sludge application.

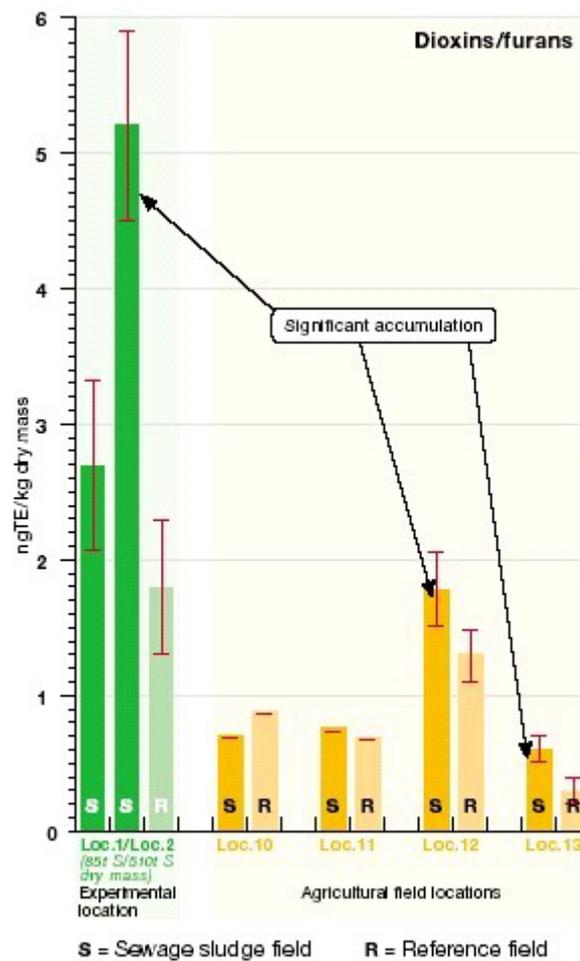
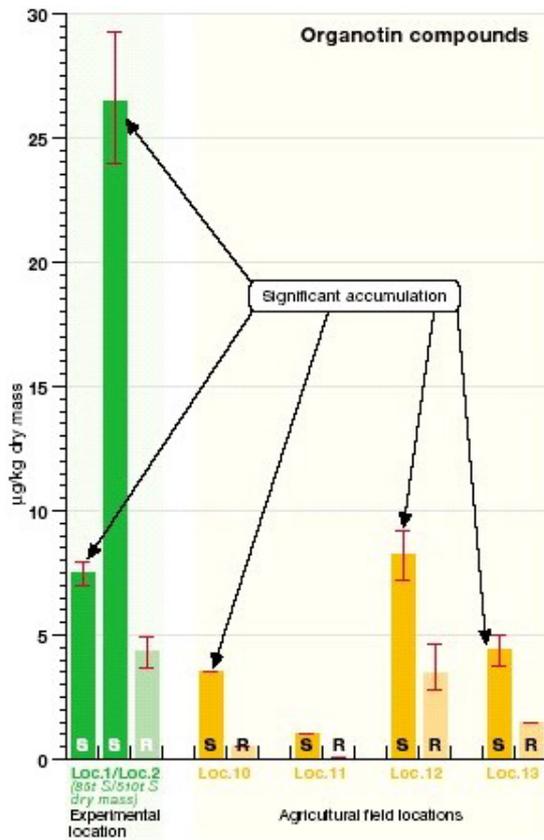
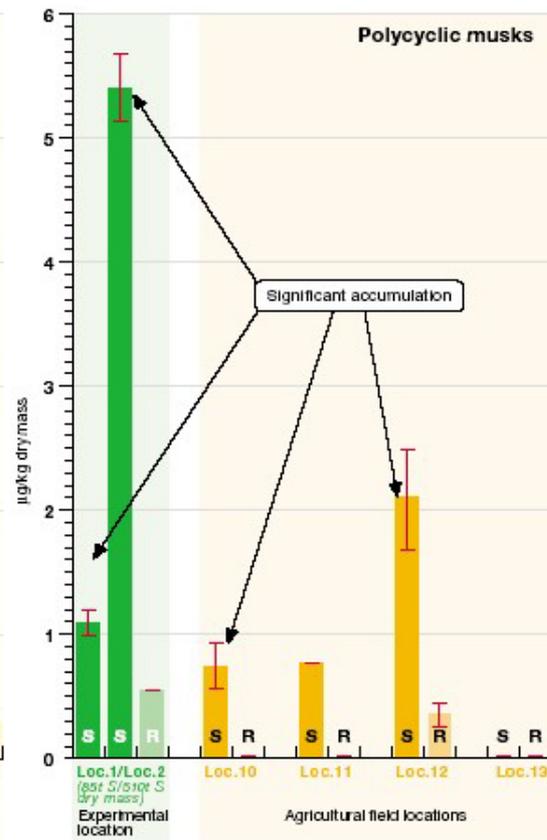


Fig. 4: PCDD/PCDF concentrations at selected locations (Values for locations 10 and 11 from single measurements)



Loc. = Location **I** = Standard Deviation

Fig. 5: Organotin compound concentrations at selected locations (Values for locations 10 and 11 from single measurements)



S = Sewage sludge field **R** = Reference field
Loc. = location **I** = Standard Deviation

Fig. 6: Concentration of the polycyclic musks HHCB + AHTN in selected locations (Values for locations 11 and 13 from single measurements)

Table 2:

Concentrations of substances and substance groups in the soil of the sewage sludge and reference fields. The values given are for soil dry mass. Those concentrations that have been derived from a single measurement are shown in brackets. The heavy metal values were derived using aqua regia extracts unless otherwise indicated. The table shows the data only for those locations that have higher concentrations of contaminants as a result of sewage sludge application.

Parameter	Units	Location 1			Location 2		Location 1/2		Location 10		Location 11		Location 12		Location 13	
		S	S	R	S	R	S	R	S	R	S	R	S	R	S	R
Cd	mg/kg															
Cd (EDTA)	mg/kg				1.1	0.4										
Cr	mg/kg				0.8	0.4										
Cu	mg/kg				37.4	22.6			43.5	33.3						
Cu (EDTA)	mg/kg				20.0	9.0			21.3	15.2			21.4	16.9		
Mo	mg/kg				1.0	0.7							7.2	5.6		
Pb	mg/kg				31.9	24.9										
Sb	mg/kg				1.0	0.6										
V	mg/kg								51.2	40.6						
Hg	mg/kg				0.8	1.7	0.5									
Zn	mg/kg				170.8	90.0			73.7	56.2			104.9	75.2		
Zn (EDTA)	mg/kg				64.8	19.0			4.9	2.6			4.8	2.5		
PCDD/PCDF	ng TE/kg				2.7	5.2	1.8						1.8	1.3	0.60	0.31
PCBs	mg/kg				0.050	0.090	0.023									
PAH	mg/kg				0.44	0.50	0.27		(0.35)	(0.06)						
OT	µg/kg				7.5	26.8	4.3		(3.3)	(0.5)	(1.1)	(n.n.)	8.3	3.6	4.4	1.4
TBT	µg/kg					1.4	0.3									
Polycyclic musks	µg/kg				1.1	5.3	0.55		0.77	n.n.	(0.80)	(n.n.)	2.1	0.3		
HCB	mg/kg					0.003	0.001									
Sum of DDT groups	mg/kg				0.006	0.008	0.003									

S = Sewage sludge field **R** = Reference field

Identification of PCB congeners of concern for a multimedia environmental risk assessment

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Abstract: Polychlorinated biphenyls (PCBs) are a group of synthetic organic compounds that have been produced in large amounts from 1930 to the late 1970s. They were widely used in a variety of industrial products and processes, e.g. for the use as flame retardants, as dielectrical fluids in the electrical industry and as additives in oils. PCBs have attracted concern because of the ubiquitous distribution, their persistence in the environment and their potential for harmful effects on human health and ecosystems. PCBs bioaccumulate and biomagnify in environmental matrices (e.g. sediments, fat tissue, etc.). Among the biological effects, damage to liver, reproductive problems, and immunotoxic responses are reported. Among the 209 possible PCB congeners, not all are of environmental concern. Criteria for the evaluation of PCB congeners of concern have been their potential toxicity, environmental occurrence and mobility.

1. Potential toxicity

Few PCB congeners exhibit acute toxicity (McFarland and Clarke 1989, Bright et al. 1995), but exposure may result in chronic adverse effects on survival, growth and reproduction (Suedel et al. 1997). For the prediction of effects, congener-specific toxicities have to be regarded (Schweitzer et al. 1997).

Acute or direct toxicity is demonstrated by PCBs which are sterically similar to 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (Bergen et al. 1996). These non-ortho substituted PCBs assume a coplanar configuration which results in a high affinity for the dioxin (Ah) receptor (Bright et al. 1995, Campfens and Mackay 1997). Other PCBs, as well those that show acute toxicity may also be involved in toxicity indirectly by inducing bioactivating enzyme systems in the liver. The biological effect of this enzyme induction is the production of toxic metabolites. The effectiveness of the compounds to induce enzymes correlates to their stereochemistry (McFarland and Clarke 1989).

PCBs of toxicological concern have been evaluated following this structure-activity relationship, encompassing a group of 73 congeners (see Tab. 1). Most effective PCBs are coplanar, mono-ortho and di-ortho congeners (group I at Tab. 1). Di-ortho PCBs are also the most important group for neurotoxic effects (US HHS 2000). Also included in the evaluated group are PCBs showing strong enrichment in the liver (Ahlborg et al. 1992) or the potential to promote tumours (US HHS 2000).

2. Environmental occurrence

Some PCB congeners of toxicological relevance are reported to show very low quantities in environmental samples (e.g., Alford-Stevens et al. 1988, McFarland and Clarke 1989, Brannon, et al. 1991, Hansen, et al. 1997, Meijers et al. 2003). To identify congeners of concern with respect to environmental frequency, literature studies have been performed. Results are PCB congener patterns of contaminated soils, sediments and other environmental samples (animal tissues, human fat and milk). Differences between these patterns are obvious.

Table 1: PCB congeners of toxicological concern (IUPAC-number), according to McFarland and Clarke (1989).

Group I	a) pure-3-MC inducers (*) PCB 77, 126, 169
	b) mixed-type MFO inducers (**) PCB 37, 81, 105, 114, 118, 119, 123, 128, 138, 156, 157, 158, 166, 167, 168, 170, 189
Group II	PB-inducers (***) PCB 47, 66, 85, 87, 99, 100, 101, 133, 137, 139, 140, 153, 154, 163, 165, 171, 180, 181, 182, 183, 184, 190, 191, 194, 195, 196, 197, 203, 204, 205, 206, 207, 209
Group III	weak PB-inducers PCB 11, 14, 15, 52, 54, 75, 80, 136, 146, 151, 155, 159

(*) 3-MC: 3-methylcholanthrene-type, (**) MFO: mixed-function oxidase, (***) PB: Phenobarbital-type.

Frequencies of PCB congeners at environmental matrices have been analysed in terms of relative abundance (percent of total PCBs in a sample). Tab. 2 shows PCB congeners that meet the criteria of toxic potential and environmental relevance (group A to C). Furthermore, congeners are listed for which no toxicity data are available but a significantly high abundance is reported (group D).

Table 2: PCB congeners of different toxic potential as a function of environmental frequency.

Group A	1) reported frequency in environmental matrices: 0.5 % of total PCB or higher
highest toxic potential	PCB 37, 77, 105, 118, 123, 128, 138, 156, 158, 167, 170, 189
	2) low frequency (<0.5 %)
	PCB 81, 114, 119, 126, 157, 166, 168, 169
Group B	frequency: 0.5% or higher
high to moderate toxic potential	PCB 47, 66, 85, 87, 99, 101, 137, 153, 180, 183, 191, 194, 195, 196, 202, 203
Group C	frequency: 0.5% or higher
low toxic potential	PCB 15, 52, 75, 80, 136, 146, 155
Group D	high frequency (> 5% of total PCB in one or more of the matrices soil, sediment and human health and animal tissues)
no toxic potential reported	PCB 8, 16, 17, 18, 20, 22, 25, 26, 28, 31, 32, 34, 41, 42, 44, 49, 50, 56, 60, 64, 70, 71, 74, 82, 90, 95, 96, 110, 132, 149, 151, 177, 187, 201

3. Mobility and transport potential

Fugacity based multimedia environmental computer modelling has been carried out to evaluate the tendency of PCBs to distribute into different compartments of a generic environment (computer program Level III, based on the publication of Mackay 2001). This model regards physicochemical properties of the contaminants, and a range of environmental descriptors (e.g., organic matter content in soil, lipid content in fish, water- and wind velocities). Presuming equilibrium conditions, contaminant concentrations in different compartments can be calculated (e.g., contaminant concentrations in soil, water, sediment phase, fish phase, air phase, aerosol).

3.1 Physicochemical properties of PCBs

Physicochemical properties of PCBs have been derived from literature studies and estimations. Taking into account all available data, inconsistencies are likely to occur. E.g., measured Henry's Law constants may deviate from those calculated from measured vapour pressure and water solubility. Therefore, values of vapour pressure, water solubility, Henry's Law constant, octanol-water and octanol-air partition coefficients have been analysed and adjusted using a procedure developed by Beyer et al. (2002). Results are a consistent set of physicochemical data, considering all available information.

3.2 Level III modelling

The input of a constant emission rate of PCB congeners into soil showed different results for soil to soil, soil to water and soil to air pathways. As it can be seen in Fig. 1, moderately and high chlorinated PCBs are predominant in the soil. In the water and air phase, low chlorinated PCBs show increased, high chlorinated PCBs strongly decreased concentrations. Therefore, high chlorinated PCBs are relatively immobile.

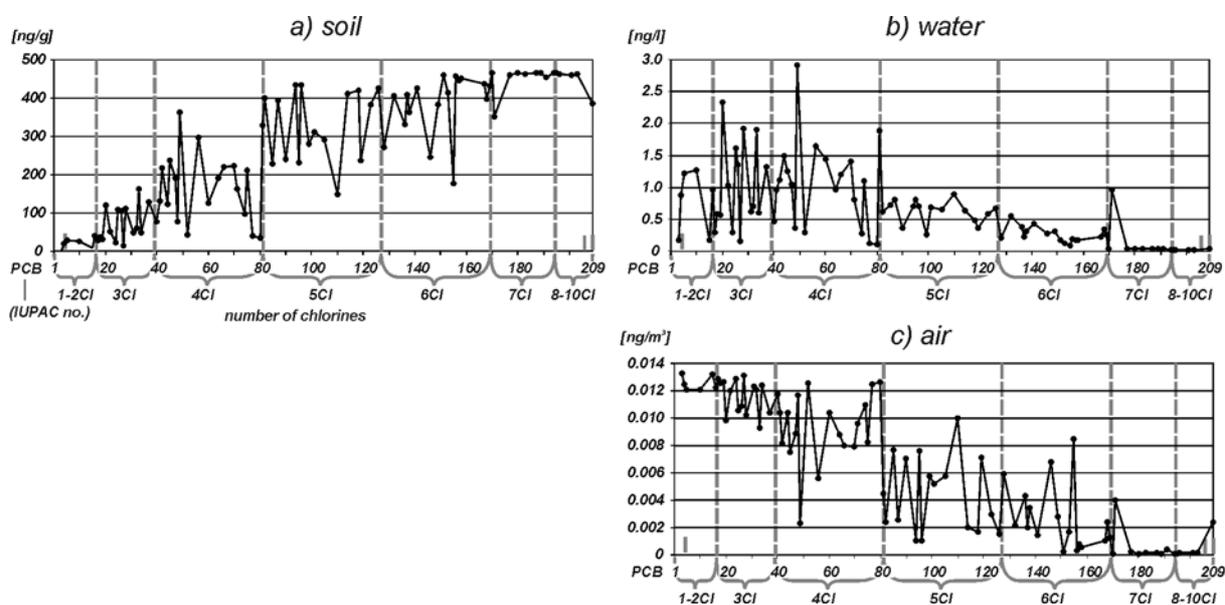


Figure 1: Results of Level III partitioning modelling, concentration of PCB congeners in different compartments of a generic environment. a) soil to soil, b) soil to water, c) soil to air pathway.

4. Results and discussion – PCB congeners of concern

PCB congeners of concern have been evaluated considering potential or actual toxicity, frequency in environmental matrices and mobility tendency (see Tab.3). Tab. 3 includes the PCB congeners presented in Tab. 2 and additional information:

- in older contaminations, low chlorinated PCBs are likely to be reduced in large scales by biodegradation (see Tab. 3, * and in parentheses),
- some high chlorinated PCBs are relatively immobile and therefore have a restricted potential for adverse environmental effects (see Tab. 3 ** and in parentheses; compare to the figure above).

Though considerable uncertainty is assigned with the biodegradation activity at a given site, moderately chlorinated PCBs are suggested to be of greatest environmental concern for a multimedia environmental risk assessment. This group contains 50 PCBs, all PCBs of concern encompass 77 PCBs.

Table 3: Evaluated PCB congeners of concern (IUPAC numbers).

<i>Number of chlorines:</i>						
2*	3	4	5	6	7**	8**
(8)	(16)	41	82	128	170	(194)
(15)	(17)	42	85	132	(177)	(195)
	(18)	44	87	136	(180)	(196)
	(20)	47	90	137	(183)	(201)
	(22)	49	95	138	(187)	(202)
	(25)	50	96	146	(189)	(203)
	(26)	52	99	149	(191)	
	(28)	56	101	151		
	(31)	60	105	153		
	(32)	64	110	155		
	(34)	66	114	156		
	(37)	70	118	157		
		71	119	158		
		74	123	166		
		75	126	167		
		77		168		
		80		169		
		81				

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SESSION II: BIOGEOCHEMICAL AND PHYSICAL PROCESSES

KEY NOTE: Preferential flow and transport – a buzzword or a problem

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Abstract: The expression 'preferential flow' has been widely used for different transport phenomena in soils. Macropore flow is only one facets of the picture (Jarvis 2002). The limited mixing in the unsaturated zone is corrupting field-measured data and lab-measured data do often not reflect the dominant processes occurring under field conditions. Flow heterogeneity requires new observation methods that provide, on one hand, data with a higher spatial resolution and, on the other hand, which allow spatial averaging of the pertinent soil data up to the relevant scale of a field. This contribution is focused on the role of preferential flow for the *mobility of sorbing solutes*.¹

1. Rapid outflow vs. preferential flow

The response to an infiltration event might be rapid for at least two different reasons, (i) because close to saturation the old water is being displaced and pushed out of the system and (ii) water might bypass the better part the old water residing in the soil matrix, or both, partly bypassing and partly displacing old water.

The degree of bypassing is essential for the increased mobility of reactive solutes.

Over the past two decades the number of papers presenting evidence of flow heterogeneity in field soils has become overwhelming (Jarvis 2002). Partial bypassing is the rule rather than the exception (Flury et al. 1994.) Depending on the soil macrostructure such as fissures, biopores, root channels, and textural boundaries the percolating water encounters very different sorbing surfaces. Applying a tracer solution onto the soil surface, either as a single pulse preceded and followed by equal water infiltration, has become a standard technique to study preferential flow under field conditions.

2. Parameterize solute mixing in soils

Preferential flow is triggered either by a spatially variable flux boundary (micro-relief, stem flow or canopy drip, irrigation, etc.) or by preferential ports of entry (burrows, cracks, depressions, or uneven textural boundaries in the soil, etc.). The modeling efforts to describe preferential flow are numerous, but those describing the initiation process of preferential flow infrequent (Weiler and Flühler, 2004). Once the infiltrating water follows preferentially certain pathways, it mixes solutes with the neighboring matrix where the less mobile water resides. This mixing process in the direction transverse to the main direction of flow is crucial process for understanding (and predicting) preferential flow.

The mixing regime is being quantified by estimating the hydrodynamic dispersion coefficient almost exclusively in the main direction of flow, and the related parameter is the longitudinal dispersivity λ_{long} . Under field conditions this mixing parameter λ_{long} increases in the majority of tested cases with transport time and distance because the exchange of solutes between the rapid flow paths and the neighboring matrix is incomplete and rate-limited. This is one of the causes why the measured vertical distribution $c(z)$ of the applied tracer deviates from that predicted with chromatographic models.

¹ This contribution is an overview on the material that I will present at this conference and covers therefore primarily (but not exclusively) our own work. It is therefore NOT an overview on the pertinent literature of this subject. The most comprehensive overview in this context is that of Jarvis (2002).

Measured $c(z)$ often exhibit a long leading tail because once a water parcel moves rapidly in a rapid flow path, it stays in this flow path over a significant fraction of the entire transport distance. The characteristic length of such continuous flow paths is in the order of the macrostructures such as soil horizon thickness, vertical extension of fissures roots and burros, vertical inclusions of finer material and many other macrostructural features. This delayed mixing is taken care of by many dual porosity or 2-region models, in which the flow in the rapid flow paths, that in the matrix, and the coupling flow between these two regions, is conceptualized. The parameter of the coupling term is mostly determined by fitting experimental observations.

In rare cases this coupling term is expressed as the transverse dispersivity λ_{trans} (Forrer et al.1999). This property λ_{trans} is the cause and λ_{long} the effect of the deviations from chromatographic behavior of solutes. The transverse dispersivity λ_{trans} discriminates the convective dispersive from the stochastic convective transport regime. To determine λ_{trans} the solute tracer must be applied as a line or point source onto the soil surface (pulse or step input). In addition, the distribution of the tracer concentrations must be observed at in at least two dimensions at a high spatial resolution. This requires imaging techniques such as the dye tracing reported by Forrer et al. (2000) and Aeby et al (2001).

Dispersivities are estimated from the spreading of the tracer, that is from the first and second spatial moments of the tracer concentration distribution $c(x,z; t)$ observed at a given time in the traced vertical soil profile. Forrer et al. (1999) showed that the ration between $\lambda_{trans}/\lambda_{long}$ is often much larger than the values of ≈ 0.1 taken from groundwater research data.

Spreading alone, however, does not capture the preferentiality of the flow paths nor the local mixing. The ideal (or complete) spatial mixing is Gaussian (“chromatographic”). Maximum mixing occurs when the third and higher order moments of the $C(x,z)$ distribution are zero where $C(x,z) = c(x,z) / M_c$ is the relative concentration and M_c the mass of the entire solute plume. The deviation from the perfect Gaussian mixing can be expressed either by these non-zero higher order moments or by the dilution index E (Kitanidis 1994, Ursino et al 2001) and by the reactor ratio R . To obtain E the entropy $[C(x,z) \log C(x,z)]$ (degree of mixing) is integrated over the plume area. The reactor ratio is $R = E_{actual}/E_{max}$, hence it characterizes the non-ideality of mixing in a given plume or the degree of preferentiality.

3. Retardation in rapid flow paths and matrix

Preferential flow paths may persist seasonally (Penfield and Centofanti, work in progress), for decades (Hagedorn and Bundt 2002, Bundt et al., 2000), or over the time scale of soil formation as for instance in pseudogleys with the whitish striation of continuously leached flow paths. X-ray tomograms showed that these whitish streaks are fissures of 50 to 80 μ m width. Vanderborght et al. (2002a and 2002b) carried out breakthrough experiment on soil columns from such pseudogleyic soils using three differently sorbing tracers (Cl^- and 2 fluorescent dyes). In a second run with the same columns they stopped breakthrough experiment after one pore volume, sliced the columns and mapped one of the fluorescent dyes in the cross sections of the slices. A double porosity model was used to predict the breakthrough curves of the two sorbing tracers based on the model calibration with Cl^- . The only way to simultaneously (re-)predict the breakthrough curves of the differently mobile tracers (notably in the subsoil columns) was assuming different adsorption isotherms for the mobile and immobile region. Since the columns had been x-rayed before the experiment we verified the nature of the rapid flow paths that were, in this case, continuous macropores. The adsorption capacity of the fissured region and its vicinity was definitely lower than that of the neighboring matrix. The reverse is known when herbicides are being selectively sorbed on the organic coatings of earthworm burrows or on the clay liners on aggregate surfaces.

4. Roots mediate preferential flow

Bundt et al. (2000) and Hagedorn and Bundt (2002) showed that the radionuclides deposited during the various fallout episodes of the past 50 years onto a forest soil occur at definitely higher activities in the preferential flow paths than in the surrounding matrix. These flow paths as well as those investigated by Vanderborght et al. (2002a+b). The presence of roots was also more abundant in the preferential flow paths. In this case the roots were many times younger than the roots, which suggest that roots follow the preferential flow paths.

Penfield and Centofanti (work in progress) investigated the Czernobyl ¹³⁷Cs in a 30-year grassland soil, which was then planted to maize. Opposite to the forest soil the ¹³⁷Cs was equally present in the preferential flow paths as in the matrix. Before planting maize a pulse of Non-Czernobyl ¹³⁴Cs was applied onto the surface. The ¹³⁴Cs followed clearly or almost exclusively the preferential flow paths imaged with a fluorescent dye but in the bare soil treatment it remained in the top few centimeters of the profile. This demonstrates that on a seasonal time scale roots may induce a network of preferential flow paths, which is highly permeable for certain strongly sorbing elements.

5. Conclusions

- If soils are close to saturation the outflow of (old) water, laterally or vertically, can be rapid but the infiltrating new water might percolate predominantly through the matrix causing a high retention of sorbing solutes.
- The flow field in soils – notably in unsaturated soils – is highly heterogeneous. Preferential flow is rather the normal case and not the exception.
- Preferential flow is particularly important for reactive compounds because the preferential flow paths might have a definitely lower or higher adsorption capacity than the bypassed matrix.
- The presence of roots is predisposing the network of preferential flow paths or following this network depending on the time scale of the structures causing the preferential flow.

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Soil water regime and its impact on transport of contaminants

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Abstract: Transport of contaminants in soil, and its intensification due to preferential flow effects, plays important role when problems related to groundwater pollution are dealt with. In structured soils, preferential flow usually develops under specific conditions. These conditions are closely related to the soil water regime, which in turn depends on weather and climate. Typical situation, during which macropores actively contribute to migration of contaminants from the soil surface to deeper soil horizons, occurs during rainstorm events, especially when rainfall intensity is greater than infiltration capacity of the soil matrix. If such conditions last for a sufficiently long period, this may result in a complete breakthrough of contaminant through the vadose zone and subsequent pollution of the underlying aquifer. One-dimensional dual-permeability model of unsaturated water flow and solute transport was used to study soil water regime at an experimental site during several growing seasons. The results were compared with the available observations of soil water pressure and subsurface water discharge. The analysis reveals well defined periods of deep percolation interspersed with longer lasting periods when soil water movement is confined to a shallow stratum below the soil surface. The deep percolation episodes represent periods of increased susceptibility to contamination from diffuse sources of pollution.

1. Introduction

In the last few decades, several models based on dual continuum approach (e.g. Gerke and van Genuchten, 1993; Vogel et al., 2000) have been developed to simulate movement of water and chemicals in soils. The models are often referred to as dual-permeability models. In these models Darcian flow assumption for the water movement and advection-dispersion approach for the solute transport are assumed to be valid for each of the two coupled domains: the soil matrix flow domain and the preferential flow domain. This allows simulation of preferential flow effects in heterogeneous structured soils.

The present paper adopts the dual-permeability approach to model seasonal soil water regime in an experimental watershed. Furthermore, scenario simulations of subsurface contamination from a potential diffuse source of pollution are carried out.

2. Material and methods

2.1 Experimental site

Experimental watershed Uhlirska is located in Jizera Mountains, North Bohemia, in an average altitude of 822 m above the sea level. The watershed belongs to humid region, where annual precipitation exceeds 1300 mm/year. The soil profile at the hillslope site of interest is shallow and highly heterogeneous. The soil was classified as Dystric Cambisol. It is formed on decayed fractured granite bedrock. The soil surface is mostly covered by grass and newly developing young spruce trees succeeding massive deforestation.

The experimental site is situated above the steepest part of the hillslope. Automated data collection devices are used for continuous monitoring of the subsurface runoff in an experimental trench (Sanda & Cislerova, 1998). The water discharge collected in the trench is measured at by tipping-bucket flowmeters. Soil water pressure is monitored at several depths by means of soil water pressure tensiometers.

Fig. 1 shows the discharge from the horizon situated about 80cm below the soil surface, as observed in the experimental trench. The discharge was measured during the summer season 2000. Note the

distinct responses to the three major rainstorms of the season. For the rest of the period much smaller subsurface discharge was observed. Similar behavior is characteristic for the watershed. This is also reflected in the stream hydrograph observed at the watershed outlet profile (not shown here).

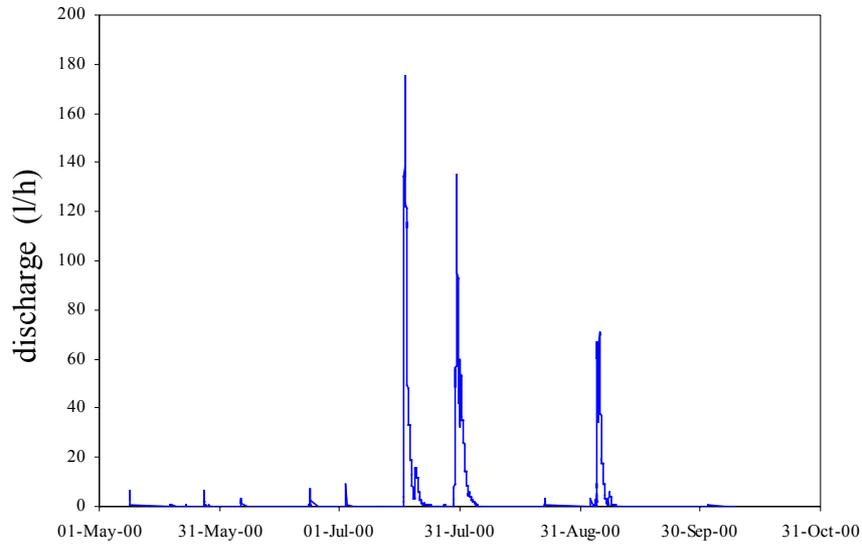


Figure 1: Observed subsurface discharge, collected in the experimental trench at the depth of about 80 cm below the soil surface; Experimental watershed Uhlirska, summer 2000

2.2 Conceptual model of flow and transport

The highly heterogeneous soil, where significant preferential flow effects were reported, is conceptualized as a dual-permeability system. Variably saturated flow in the soil profile is described by means of two coupled Richards' equations. Water transfer between the matrix and the preferential flow domain (further referred to as PF-domain) is assumed to be proportional to the pressure head difference between the domains through a first-order transfer term. Similarly to the water flow, the solute transport is described by means of two coupled advection-dispersion equations (Gerke and van Genuchten, 1993):

$$\begin{aligned} \frac{\partial \theta_f c_f}{\partial t} + \nabla \cdot (\mathbf{q}_f c_f) - \nabla \cdot (\theta_f \mathbf{D}_f \nabla c_f) &= P_f - \frac{\Gamma_s}{w_f} \\ \frac{\partial \theta_m c_m}{\partial t} + \nabla \cdot (\mathbf{q}_m c_m) - \nabla \cdot (\theta_m \mathbf{D}_m \nabla c_m) &= P_m + \frac{\Gamma_s}{w_m} \end{aligned} \quad (1)$$

where θ is water content ($\text{cm}^3 \text{cm}^{-3}$), c is concentration of a transported substance in water ($\mu\text{g cm}^{-3}$), \mathbf{q} is volumetric flux of water (cm s^{-1}), \mathbf{D} is the tensor of hydrodynamic dispersion ($\text{cm}^2 \text{s}^{-1}$), and P is a source/sink term ($\mu\text{g cm}^{-3} \text{s}^{-1}$) – equal to zero for conservative transport, Γ_s is the solute transfer term, w_m and w_f are volume fractions of the matrix domain and PF-domain, respectively. The solute transfer is defined as the mass flux of solute transported from one domain to the other, and is expressed by:

$$\Gamma_s = \Gamma_w c_i + \alpha_s (c_f - c_m) \quad (2)$$

If water flows from the PF-domain to the matrix, then $c_i = c_f$, for flow in the opposite direction: $c_i = c_m$. The first term on the right hand side of (2) defines the advective exchange of solute due to the transfer of water from one domain to the other, Γ_w , caused by the pressure difference between the two

domains. The second term accounts for the diffusive exchange of solute due to a concentration difference.

2.3 Simulation of soil water flow

The above mentioned governing equations can be solved using one-dimensional dual-permeability model S 1D Dual developed at the Department of Hydraulics and Hydrology CTU FCE, based on earlier single-permeability code HYDRUS 5 (Vogel et al., 1996). S 1D Dual was used to study soil water dynamics throughout selected summer seasons of the period 1997 - 2003. In this paper, only the results obtained for the year 2000 are discussed.

The model was used to simulate vertical soil water movement in the soil profile. The top boundary condition for water flow was natural rainfall observed between May 1 and October 31, 2000. The estimated potential transpiration was taken into account through the root water uptake function. Soil hydraulic parameters for the matrix domain were determined from the available laboratory undisturbed core sample measurements of soil water retention curves and saturated hydraulic conductivities. The PF-domain properties were estimated based on the laboratory column inflow/outflow experiments. Complementary information was obtained from the MR imaging of water flow in undisturbed soil samples (Cislerova et al., 2002). In addition, upscaling of soil hydraulic properties from the laboratory scale to the field scale was also performed.

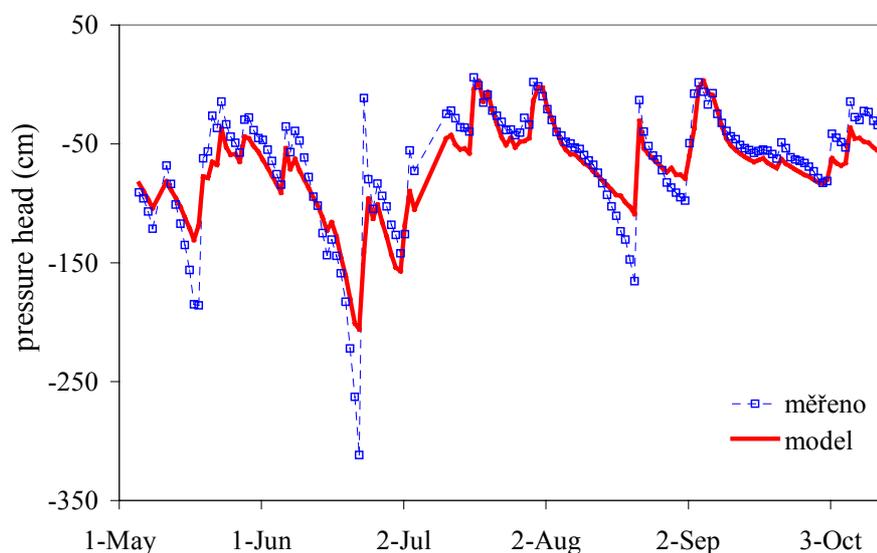


Figure 2: Comparison of the pressure head observed by tensiometer (inserted in depth of 24 cm below the soil surface) and the corresponding pressure head simulated by the numerical model; Experimental watershed Uhlirska, summer 2000

2.4 Simulation of solute transport

In the next step, the dual-permeability model was used to study the transport of potential surface contamination throughout the soil profile. Commonly used pesticide atrazine was used in solute transport simulations as an example of a possible source of diffuse pollution.

Initially, the pesticide was limited to the 1cm layer below the soil surface. The spreading of the contaminant during the period of summer season 2000 was simulated by the model. The pesticide is transported mainly by advection. At the same time it is subject of hydrodynamic dispersion, linear equilibrium sorption and first order decay.

Three transport scenarios were considered. First, steady state water flow in a single-permeability system was assumed. This highly idealized approach is quite often used in various subsurface

contamination studies. It is included here as a reference case. For this scenario, the steady state soil water flow velocity was obtained by averaging the transient discharge from the soil profile.

Second scenario was based on a standard unsaturated flow approach. Transient soil water velocity field is in this case obtained by solving Richards equation for a single-permeability system, taking into account hourly variation of rainfall and evapotranspiration intensities.

Third scenario involves transient water flow conditions in a dual-permeability system. In this case, it was assumed that all sorption takes place in the matrix domain and none in the PF-domain.

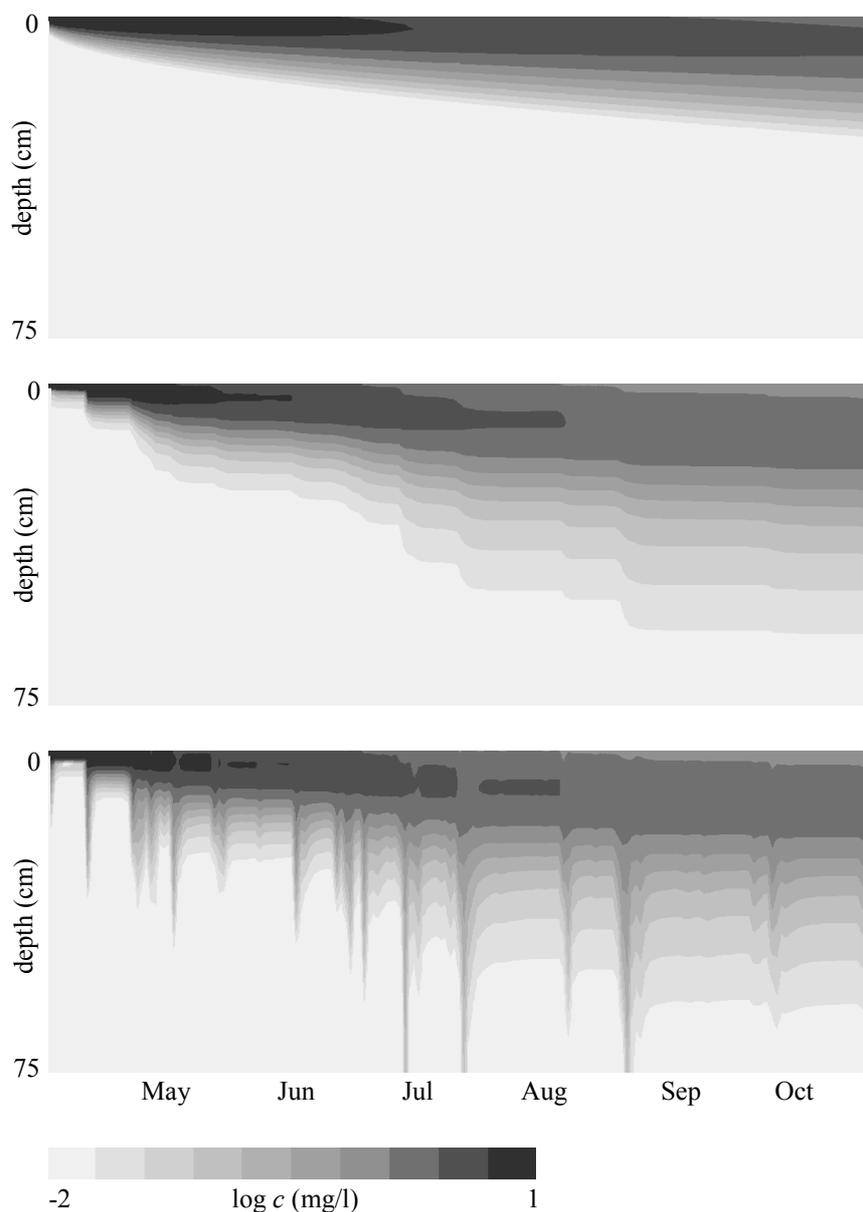


Figure 3: Three scenarios of the contaminant transport: (a) single-permeability system under steady state water flow conditions, (b) single-permeability system under transient flow conditions, (c) transport in the preferential flow domain of the dual-permeability system under transient flow conditions

3. Results and discussion

Fig. 2 shows one of the soil water pressure observations. The pressure sensor was situated in the vicinity of the experimental trench, at the depth of 24 cm below the soil surface. The observed values are compared with the corresponding pressure head variations computed by the numerical model. Although the match between the observed and simulated values is not perfect, it indicates an overall agreement in behavior of the real and model system.

The results of simulated solute transport scenarios are summarized in Fig. 3. It is obvious that in both scenarios dealing with single-permeability system the depth of penetration of the contaminant is seriously underpredicted. This is especially true in the case of the reference scenario, based on steady state water flow assumption. The third, dual-permeability, scenario predicts significant breakthrough of contaminant through the preferential flow domain of the soil profile.

4. Conclusion

The presented simulation scenarios show the importance of the adequate conceptual model of flow and transport for prediction of subsurface migration of contaminants in the vadose zone. In particular, the issue of enhanced mobility of subsurface pollution in response to episodic rainstorm events is addressed.

5. Acknowledgements

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Preferential flow as a source of fast transport in the vadose zone of the Czech Upland Basins

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1. Introduction

At about 60% of the soils in the Czech Basin has been formed on decayed crystalline bedrocks as a result of weathering process, and belongs to the class of Dystric Cambisols. Wide range of particle size distribution of these soils creates conditions for the flow irregularities, namely the occurrence of preferential flow and the flow parameters instability. From the results of a large number of field and laboratory experiments there is evidence that mentioned effects are born already at the scale much smaller than a standard experimental sample size to determine soil hydraulic functions. In the engineering practice the standard undisturbed soil samples represent the scale of REV, as a volume/area used in the averaging process. The spatial variability is commonly analyzed for a set of values measured on the samples in the lab. It cannot express the impact of microscopic preferential flow and flow instability, because these effects have been already smeared. There is a need to study in detail also processes connected with internal heterogeneity within the standard soil samples. The appropriate upscaling should help in more realistic mathematical simulation of natural flow and transport processes in the vadose zone.

2. Tools for preferential flow and solute transport simulation

The theoretical inadequacy of the use of traditional Richards' equation (RE) has been discussed from different points of view (e.g. Nitao a Bear, 1996, Feyen et al., 1998, Císlarová, 1999). Straightforward improvements consist in alternative expression of soil hydraulic parameters to be used in RE. Compared to standard van Genuchten's approach also parameters describing the soil structure are included (Assouline et al., 2001). For soils with a higher air entry value a stochastic description of porous media by means of overlapping sphere volumes (Chan a Govindaraju, 2003) has been introduced.

Fast flow and solute transport in vadose zone denoted usually as preferential flow is however more complicated process. An impact of the dynamics of flow on the soil hydraulic characteristics has been found in a number of experiments (Hassanizadeh et al., 2002). Two phase character of simultaneous flow of water and air in heterogeneous soil materials is practically impossible to describe using multiphase simulation models since the air phase often exhibits discontinuities in forms of residual air enclosed in pores by flowing water and leads to flow instability (Fabysenko, 1995). Usually these effects are very difficult to detect because are not captured in tensiometer measurements. During recurrent ponded infiltration - outflow experiments on undisturbed soil samples performed in nuclear magnetic resonance (MR) scanner such behaviour was clearly detected (Císlarová et. al., 2002, Císlarová a Votrubová, 2002, Votrubová et al., 2003).

A promising approach to simulate preferential flow and transport derives from the principle of dual permeability concept (Gerke a van Genuchten, 1993, Vogel et al., 1993, Jarvis, 1994, Flühler et al., 1996, Germann a Di Pietro, 1999, Vogel et al., 2000). In the simulation model of Vogel et al. (1993) implanting the idea of Gerke and van Genuchten (1993) the heterogeneous flow domain is splitted into two macrocontinua. One represents the fast flow domain capturing preferential flow; the second one corresponds to the flow in the soil matrix. In this model two RE are thus solved, independently for each subdomain. Mutual interaction of both domains is maintained by a special transfer term.

3. Materials and Methods

As mentioned above, in coarse sandy loam soil profiles overlaying crystalline bedrocks, typical for the Czech Basin, fast preferential flow forms in a consequence of the internal heterogeneity of the soil matrix (Císlarová et al., 1988, 1990). It rapidly propagates through the watershed contributing the early outflow formation. As a representative, the Korkusova Hut (KH) coarse sandy loam (Dystric Cambisol) was the soil under study (Císlarová et al., 1988, 2001). Considering the key information regarding solute transport, the flow rates, relying on standard experiments they stay significantly underestimated for this type of soil (see Fig. 1). The possibility to determine reliable flow cross-section area together with its potential changes in time has been studied by means of noninvasive visualisation of potential flow paths. CT images were used to analyze the soil structure; MR imaging was applied to trace volumes of water flowing through the soil sample during the experiment. In all experiments the simple vertical infiltration-outflow through undisturbed soil samples of various sizes was performed. The upper boundary condition on the top of the sample, or ponding, or fixed low suction head constant in time was maintained using tension infiltrometer disk; free outflow through the bottom of the sample was collected supplying data for seepage face boundary condition for further inverse simulations (Dohnal et al, 2004). In addition the suction heads within the soil samples were controlled by tensiometers; the weights of the sample, of the inflow and of the outflow volumes were recorded in time. The collection of all data was fully automated with very short pace to collect all changes of water balance in detail; the temperature was kept constant at 20°C (Sněhota et al., 2002).

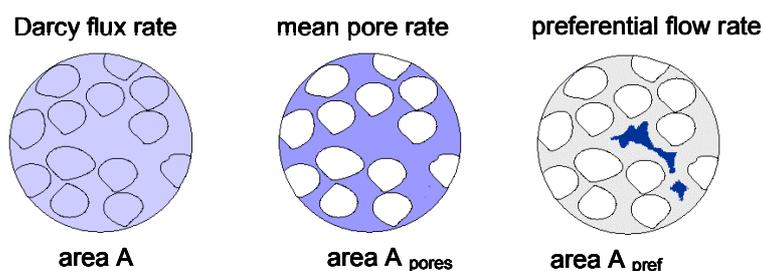


Figure 1: Flux rate averaging, $area A > A_{pores} \gg A_{pref}$

4. Results and Discussion

During the MR imaging of ponded infiltration outflow experiment several important features were observed, partly they are summarized in following points:

1. Only a portion of the empty or less dense voxels of the sample which represented potential preferential pathways was filled with water during infiltration, in other words the CT information about the dry sample density distribution is not enough for the determination of the flow regions (Votrubová et al., 2003)
2. For the soil under study MR imaging supplies information only about the water obtained in large pores. In the cross section area of the sample in the direction perpendicular to the direction of flow the averaged ratio of voxels containing visible water is about 30%. The selection evaluating the signal intensity was done by means of T_1 mapping (Císlarová et al., 1999, Votrubová, 2002, Sněhota, 2003).
3. It was detected that for the heterogeneous soil samples under study fast preferential flow forms already at the pore scale due to gravity driven flow through large pores.
4. Not all water driven by gravity drains when the infiltration stops.
5. The “steady state” infiltration rate depends on the initial saturation of the sample. The higher initial saturation of the sample means less volume flowing through the sample preferentially.

6. In repetitive (consequent) infiltration experiment only a portion of previous flowing volume was moving through the sample. When distributions of water in particular voxels during the first and second infiltration run were compared it was found that in each case water was filling different voxels (Císlarová et al., 2002). This was found in all MR infiltration experiments. Also the volumes of water drained out of the sample after each infiltration run were different and remaining visible water was differently spatially distributed (Votrubová, 2002, Sněhota, 2003).
7. The total volume of fast flowing water during the “steady state” was decreasing in time while the total weight of the sample was increasing, documenting the changing driving force field between gravity and capillarity driven volumes (Císlarová et al., 2002).
8. The main reason of the detected effects seems to be the discontinuous air phase distributed and partially closed within the sample in combination with in several orders uneven pore velocity field. The largest pore rate values are in a range of seconds remaining to the fast gravity flow in continuous large pores, the slowest ones are in a range of several days overlapping thus the time scale of the experiment and responsible for continuing redistribution even during the so called “steady state” flow. That means that very small volumes keep flowing very slowly inside of the sample, negligibly influencing the water balance but continuously changing the local driving force field distribution.

Some information of the large set of collected data was applied in inverse modelling of infiltration outflow experiments based on dual permeability principle to determine parameters of the soil hydraulic properties of the both flow domains (Dohnal et al., 2004). The flow instability has stayed untreated, additional experiments are in progress.

The knowledge was used in the large scale simulations of the hillslope outflow at the experimental area Tomšovka (Šanda a Císlarová, 2000) where the components of water cycle related to the subsurface flow are monitored in detail since 1997. In Fig. 2a the result of the hillslope outflow simulation based of standard Richards’ approach is shown. Relatively good timing of the outflow peaks is in contrast with the overestimated flow volume. Application of the dual permeability approach improves the agreement of the simulated and measured outflow significantly (Fig. 2b).

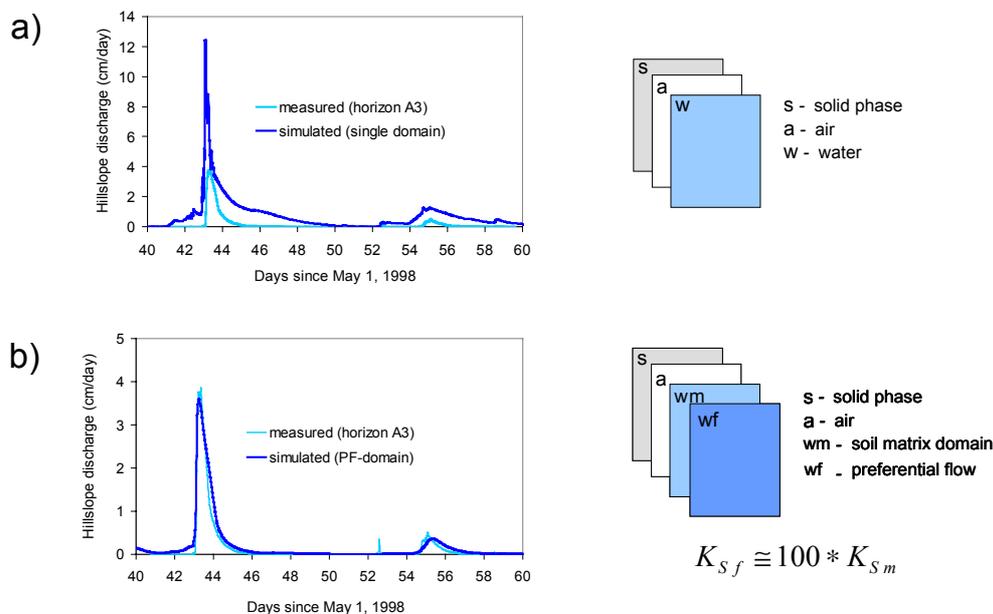


Figure 2: Single domain (case a)) and dual permeability domain (case b)) simulations of the outflow in the Tomšovka hillslope experimental area in the watershed Uhlířská

5. Conclusions

The purpose of this contribution is to inform the SOWA audience about complex work done at CTU in Prague towards better understanding to the dynamics of flow in heterogeneous natural soils to be used in construction of more appropriate simulation tools and upscaling methods. The major part of the work has been published, as cited. The most interesting results of MR visualisation will be shown during the oral presentation. The obtained data have served as inputs in inverse modelling to determine the flow parameters for dual permeability models (Dohnal et al., 2004). It represents a basic information needed to simulate solute transport processes in the areas where the preferential flow contributes to the formation of outflow (Vogel, 2004).

6. Acknowledgements

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Bacteria as bioavailability enhancing agents

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Although limited bioavailability appears to be primarily a physical, i.e. mass transfer-controlled process, different recent observations indicate that organism-specific bioavailability-enhancing strategies may exist and that generalizations about the bioavailability of sorbed, solid or dissolved substrates are inappropriate. Several reports, using polycyclic aromatic hydrocarbons (PAH), indicate that sorption-limited bioavailability plays an important role in the selection of PAH-degrading bacteria and that different PAH-degrading bacteria inhabiting the same soil may be adapted to different degrees of PAH-bioavailability. In these studies, different bacterial strains or microbial assemblages were selected depending on how the compound was provided to the bacteria (Tang et al., 1998; Bastiaens et al., 2000; Friedrich et al., 2000). This indicates that the physiology of a bacterium or its particular life style might play an important role in its adaptation to degrade HOC by providing a strategy for enhancing the compound's bioavailability.

Bioavailability for degradation of hydrophobic organic pollutants is an interactive process that is determined by the rate of physical mass transfer to microbial cells relative to their intrinsic catabolic activity (Bosma et al., 1997). Bioavailability can be conveniently described by the bioavailability number, B_n , (Koch, 1990), which is defined as the capacity of an organism's or a population's environment to provide a chemical, divided by the capacity of the organism or population to transform that chemical. This definition points at the importance of continuous substrate supply for consumptive processes and distinguishes bioavailability for degradation from bioavailability for basically 'non-consumptive' processes such as poisoning or inhibition. At high mass transfer rates, the overall degradation rate is controlled by the metabolic activity of the bacteria, i.e. the specific activity of the cells and the population density ($B_n > 1$). Conversely, when the transport of the substrate decreases or the bacterial population grows, mass transfer may become the factor that controls the degradation ($B_n < 1$). As bacteria appear to degrade chemicals only when they are dissolved in water, mass transfer to the cells in the aqueous phase is best described by Fick's first law of diffusion (eq. 1), whereas bacterial transformation is suitably described by the whole-cell Michaelis-Menten kinetics. According to Fick's law, the diffusive mass flux of a substrate towards the cell surface J is affected by the effective diffusion coefficient (D_{eff}), the space coordinate in direction of the transport (∂x), and the concentration difference between cell surface and the substrate source (∂C):

$$J = -D_{eff} \cdot \partial c / \partial x \quad (1)$$

In presence of bacteria, steady state is to be expected when solid or non aqueous phase (NAPL)-bound PAHs provide a source and bacteria act as a sink, i.e., when the bacterial consumption of PAH drives the dissolution of PAH from the source (Harms and Wick, 2004). It should be noted, however, that when coupled to microbial degradation, the actual diffusion flux is not inversely proportional to the distance, as equation (1) would suggest. Bacteria are not perfect sinks and, as illustrated by the Michaelis-Menten relationship, the aqueous substrate concentration at their cell surface rises somewhat with increased mass transfer thereby partly diminishing the gradient.

Experimental evidence and theoretical considerations show that specific bacteria degrading hydrophobic organic contaminants may adapt to low substrate regimes by the utilization of bioavailability enhancing strategies, in order to create steep concentration gradients and concomitant fast diffusive substrate transfer. Bacteria may increase the substrate bioavailability (i) by reducing ∂x between pollutants and bacteria (by adhesion to sorbents), (ii) by causing active transfer of pollutant

into the aqueous phase by production of biosurfactants and bioemulsifiers (optimization of D_{eff}), and (iii) by using uptake systems with high specific affinity, i.e. exhibiting efficient substrate degradation at low aqueous concentrations (reduction of the concentration leading to an increase of ∂C).

By using the poorly water-soluble solid polycyclic aromatic hydrocarbon anthracene as sole carbon source, we examined the possible role of bioavailability-promoting strategies in anthracene degradation by *Mycobacterium* sp. LB501T in batch cultures (Wick et al., 2002a). When solid anthracene served as sole carbon and energy source, *Mycobacterium* sp. LB501T grew as a confluent biofilm on the anthracene crystals. As shown in eq. 1, a small distance between a biofilm and a solid substrate favours the diffusive mass transfer and, consequently, the bioavailability of anthracene. Moreover, biofilm cells appeared to consume most of the dissolving solid anthracene as was seen from very low dissolved anthracene concentrations in the bulk medium. Cells at the crystal surfaces “etched” craters in the crystals due to consumption-driven PAH-dissolution on a micro-scale. Biofilm formation by strain LB501T seems to be a well-regulated process as no biofilm was formed on anthracene in the presence of alternative, soluble carbon sources or when high amounts of solid anthracene, leading to high substrate fluxes, were supplied. Adhesion of bacteria to surfaces is believed to be mediated by long-ranging colloidal interactions, which hold bacteria at the close proximity of surfaces, thereby facilitating short-ranging hydrophobic interactions and adsorption of cell surface polymers to the surface. The extent of these interactions, and particularly of the hydrophobic interactions depends strongly on properties of the interacting cells and surfaces. The cell surface hydrophobicity as a key parameter for adhesion is often expressed as the contact angle (Θ_w), i.e. the angle included between the tangent plane to the surface of a drop of water and the tangent plane to the surface of a layer of bacteria. Preferences of hydrophobic bacteria ($\Theta_w > 70^\circ$) for hydrophobic surfaces may explain the finding that particularly hydrophobic bacteria were isolated when hydrophobic membranes were used to extract them from soil instead of using a conventional water extraction protocol (Bastiaens et al. 2000). Studies on *Mycobacterium* sp. LB501T that was isolated this way have shown that bacteria may specifically respond to the low aqueous solubility and low bioavailability of anthracene by modifying their cell envelope (Wick 2003a). Anthracene-grown cells exhibited a higher cell surface hydrophobicity and adhered up to 70-fold better to hydrophobic surfaces than glucose-grown cells (Wick et al., 2002a). In general, it was found that mycobacteria growing on poorly water-soluble substrates exhibited later eluting, more hydrophobic long-chain fatty acids (mycolic acids) in their outer cell wall than cells grown on glucose (Wick et al., 2002b, Wick et al. 2003a). This finding is of interest, as mycolic acids are believed to stimulate attachment to hydrophobic surfaces and hence increase access to hydrophobic substrates (Bendinger et al., 1993). Mycolic acids, which contribute up to 60% of the dry mass of the cell wall, may also significantly increase the sorption of hydrophobic substrates to the cell envelope. Several studies have shown that sorption processes to bacterial biomass may highly influence the distribution and fate of hydrophobic substrates in the environment, for instance by giving rise to bacteria-facilitated transport (Bellin and Rao, 1993). The importance of biofilms as possible sink for dissolved organic and inorganic matter was investigated by others: It was found that, despite of their hydrogel-like character (96-98% water), biofilm extracellular polymeric substances (EPS) contained about 60-70% of all extracted BTX (benzene, toluene, and xylenes), whereas the cells contained less than 20% of the BTX (Späth et al., 1998). It is thus likely that hydrophobic cell envelopes act as transient reservoirs of hydrophobic substances. Studies on membrane-bound PLFA- and GLFA of *Mycobacterium* sp. LB501T further indicate that *Mycobacterium* sp. LB501T is specifically adapted to the growth on this poorly water soluble substrate. Despite of the low aqueous solubility of anthracene no distinct signs of stress, such as increased fractions of cyclopropyl or saturated fatty acids, of anthracene-grown cells as compared to glucose-grown cells were detected (Wick et al., 2003b). Seen the observation that mycobacteria belong to one of the few taxonomic groups responsible for PAH degradation in soils, this finding thus is not far-fetched.

No production of biosurfactants was observed. *Mycobacterium* sp. LB501T however, exhibited a high specific affinity ($a_A^0 = 32500 \text{ L g}_{\text{protein}}^{-1} \text{ h}^{-1}$) for anthracene. The specific affinity is defined by the slope of the first-order part of the whole-cell Michaelis-Menten uptake-rate versus concentration plot (Button, 1991). A high a_A^0 allows reducing the substrate concentration at the bacterial surface in

relation to the bulk aqueous substrate concentration and thus leads to steep concentration gradients and fast diffusive substrate transfer. The observed value is up to 1000 times enhanced as compared to other PAH-degraders and indicates that *Mycobacterium* sp. LB501T is well-adapted to the naturally occurring low range of aqueous anthracene concentrations ($C_w^{\text{sat}} = 3.47 \times 10^{-7} \text{ mol L}^{-1}$).

In addition, *Mycobacterium* sp. LB501T exhibits low requirements for cell maintenance. Although low maintenance coefficients do not directly affect the bioavailability, i.e. increase mass transfer to and into the cell, respectively, they may form a specific ecological advantage of a pollutant degrading community to build up an active biomass (Pirt, 1965). A low maintenance rate thus characterizes the ability of a microorganism to survive and to grow on a very low amount of substrate consumed per unit time: The less substrate an organism needs to survive, the better it is equipped to survive periods of famine and the better it is also capable of building up active biomass under a low-substrate regime, which may respond quickly to newly available pollutants and thus enhance the bioremediation efficiency.

It thus that microorganisms have evolved various strategies to obtain essential chemicals. Evolutionary adaptations support the peculiar mechanism of microbial nutrition, i.e. uptake of compounds via a passage through the cell membranes. The acquisition and assimilation of bio-elements are the most fundamental processes in an organism's struggle for life. It is therefore obvious that in complex natural systems the competition between thousands of species for limited quantities of a small number of elements is a major evolutionary factor. However, the individual contributions of the physical and biochemical aspects of nutrition to the fitness of an organism are still widely unknown. The frequent observation that biodegradation processes, e.g. in soil remediation, are limited by physical obstacles to substrate acquisition, rather than by biochemical incapacities, points at the importance of substrate mobilization strategies such as attachment and biofilm formation of *Mycobacterium* strain LB501T to optimise the bioavailability of poorly water soluble anthracene.

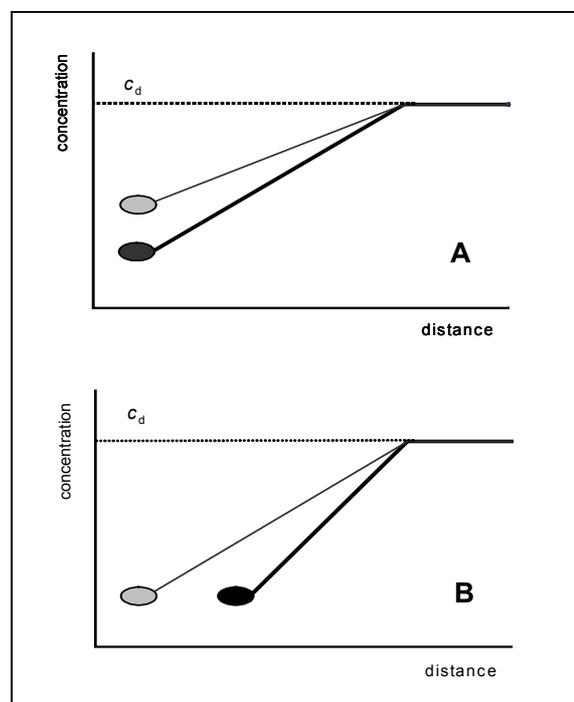


Figure 1: Schematical visualisation of how increased specific substrate affinity resulting in (A) lowered cell surface substrate concentration and (B) closer approach to a substrate source (e.g. by attachment to the substrate) steepen concentration gradients and thereby increase the diffusion flux from a substrate source.

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Olive mill wastewater :a source of microbial and phyto-toxicity for soil

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1. Introduction

Sustainable disposal of Olive Mill Wastewaters (OMW) is a serious problem in Mediterranean countries, where olive oil production is widespread.

OMW consists of the water originating from the drupae (vegetation water), process water (added to improve oil separation during milling), and washing water of olives and milling plants. OMW have high phenolic content (1.2-2.4%) and COD (50,000-200,000 mg/L). Main OMW organic compounds are sugars, pectins, tannins, organic acids, polyalcohols, lipids, nitrogen compounds, polyphenols and a brown pigment ("catecholmelaninic" polymers) (Ranalli 1987).

In the '80, most of smaller olive milling plant disappeared and were replaced by large plants with high capacity of daily processing (more than 2,000 kg of olives). The transition from the traditional, discontinuous plants to the modern, continuous ones that need higher amount of process water, gave rise to a huge increase in annual OMW production. Currently, olive milling is followed by a huge OMW production during a short time in small areas, due to seasonal olive availability and to the conveyance in the large olive mills (about 0.4-1.1 m³ of OMW are produced per ton of olives). Such large amounts cannot be disposed in water bodies without treatments.

Since the '80, different physico-chemical treatments (based on reverse osmosis, single, double and triple effect evaporation, thermocompression, drying, treatment with lime and flocculants) and biological treatments (both aerobic and anaerobic) have been studied (Ranalli 1989, Rozzi and Maipei 1996). Due to the high related costs, the physico-chemical and biological treatments have not achieved wide diffusion except for demonstrative pilot plants.

Therefore, the traditional solution of spreading OMW onto the agricultural soil continues to be applied. The agronomic utility of OMW spreading onto the soil has been hypothesized (Carlini 1992, Proietti et al. 1995, Amirante 1996, Di Giovacchino et al. 2000, Tomati et al. 2000). In this case, the high COD is not so problematic as for disposal in water bodies and can also be exploited to increase the organic fraction of poor soils. However, OMW spreading onto the soil could be responsible of a continuous decreasing of soil quality and fertility, because of their anti-microbial activity and phytotoxicity. OMW toxicity is usually attributed to the high polyphenol content (Pérez et al. 1992).

Eventually, notwithstanding the opposing opinions (Ranalli 1989), the "agronomic reuse" approach has been enforced by the current Italian legislation. OMW spreading must be carried out ensuring uniform distribution over the entire field area in order to avoid draining. Furthermore, the spreading should not exceed the amount that can be included into the soil because aquifer pollution by phenolic compounds in OMW spreading areas is a real risk (Spandre and Dellomonaco 1996).

It is probable that the effect of spontaneous remediation observed in the spreading of moderate OMW amount is due to the oxidative polymerization promoted by abiotic and biotic soil components (Colarieti et al. 2002). The effective removal of the polyphenols is ensured if dissolved oxygen is present in sufficient amounts.

Target of this work is to evaluate how the reactions involving polyphenols affect microbial- and phyto-toxicity of OMW when spread onto the soil. If natural attenuation of polyphenols is sufficient for toxicity removal, the OMW fertirrigating potential can be exploited. At the same time, an effective polymerisation of polyphenols, followed by precipitation and immobilisation in the humic fraction of soil, can prevent aquifer pollution.

2. Material and Methods

Olive mill waste waters were obtained from a discontinuous, two-phase press mill. Agricultural soil samples came from an uncontaminated field.

For the slurry experiment, 200 mL of OMW were mixed with 60 g of soil in a shaking flask. The slurry was kept stirred and aerated for 24 h. After removal of soil and OMW debris by centrifugation and filtration, residual phenolics in the supernatant have been quantified by reversed phase HPLC-UV. (Eclipse XDB-C18 column, 250 mm, mobile phase: acetonitrile (15%), water (84.7%), acetic acid (0.3%), flow rate 1 mL/min). Phenols have been identified by comparison with the retention times of standards. Unretained (hydrophilic) compounds (retention times less than 3 min) have been identified as proteins and catecholmelaninic polymers.

Phytotoxicity was evaluated by the effect on the germination of *Lepidium sativum* seeds. 20 seeds were spread on Whatman #1 filter disc imbibed with 5 mL of the liquid fraction of the slurry system (obtained by centrifugation and filtration of the supernatant) or directly on the soil-polymers mixture (recovered as the centrifugation pellet). Seeds were incubated for 3 days at 25°C in a humidity-controlled chamber. The Germination Index was calculated by the formula: $GI(\%) = (GS/GS_{\text{control}}) \cdot (RL/RL_{\text{control}}) \cdot 100$, where GS is the average number of germinated seeds, LR is the average radical length, and the subscript “control” refers to control tests with distilled H₂O.

Antimicrobial activity was evaluated by the inhibitory effect on the growth of *Bacillus cereus*. Toxicity tests were performed at 37°C by mixing 0.5 mL inoculum with 22 mL diluted wastewater and 2.5 mL of concentrated medium containing peptone (50 g/L) and malt extract (30 g/L). The reference growth curve was obtained by substituting the wastewater with an equal amount of distilled water. Growth was monitored by measuring turbidity at 600 nm.

3. Results and Discussion

Reactions involving phenolics and soil compounds were studied by slurry experiments. Main polyphenols in the OMW sample were hydroxytyrosol, catechol, and tyrosol. A complete conversion of initial phenolic content can be observed after 24 h from soil addition (Fig.1).

Before soil contact, phytotoxicity and microbial toxicity of OMW are quite strong and a high dilution of the wastewater is needed to observe germination of the seeds or growing of bacteria. As regards microbial toxicity, a zero specific growth rate is still measured with 1:4 dilution, whereas for phytotoxicity a GI of 11.6% is observed with 1:10 dilution.

After 24 h of soil contact, when all the identified phenols have been converted, undiluted OMW is still highly toxic. A reduction in microbial toxicity is apparent with 1:4 diluted OMW: the specific growth rate increases from 0 to 0.94 h⁻¹ (but still less than non-limited value of 1.80 h⁻¹). A reduction in phytotoxicity is observed with 1:10 dilution of OMW supernatant: the GI increases from 11.6% to 20.6%.

At the same time, the soil kept in contact becomes itself phytotoxic with a GI decrease from 100% to 0%. If the polluted soil is washed with 200 mL distilled water, then the phytotoxicity is reduced (GI 51.5%). At the same time, the washing water is found to be quite toxic (GI 16.3%) even though no polyphenol can be detected by HPLC analysis.

Further germination tests were performed in order to check if the reaction products of polyphenols show any phytotoxicity. Pure catechol and tyrosol solutions were used at the same concentration found in the OMW. A fast conversion of catechol can be observed if 200 mL of a 0.151 g/L catechol solution is mixed with 60 g soil. A slower conversion of tyrosol can be observed using a 0.221 g/L solution and the same amount of soil per slurry volume. In both cases a complete conversion of initial phenolic content can be still observed after 24 h reaction and final reaction products are insoluble polymers whose structure is similar to those of humic and fulvic acids (Colarieti et al. 2002).

Germination tests were performed separately for the liquid fraction of the slurry system and for the soil-polymers mixture. In both cases no phytotoxicity was detected. On the contrary, for the soil-

polymers mixture, the GI was found even higher than that recorded for the same seeds germinating on the uncontaminated soil. These results allow to conclude that polymeric compounds, obtained by the reaction of phenolic compounds with soil components, can be healthy for seeds germination, thus confirming the hypothesis that their structure is similar to that of humic and fulvic acids.

This means that other non-phenolic compounds are also responsible of the residual phytotoxicity shown by OMW-soil mixture after 24 h contact time. Such results are in contrast to the common opinion that phytotoxicity is mainly due to the high content of phenolic compounds in the OMW.

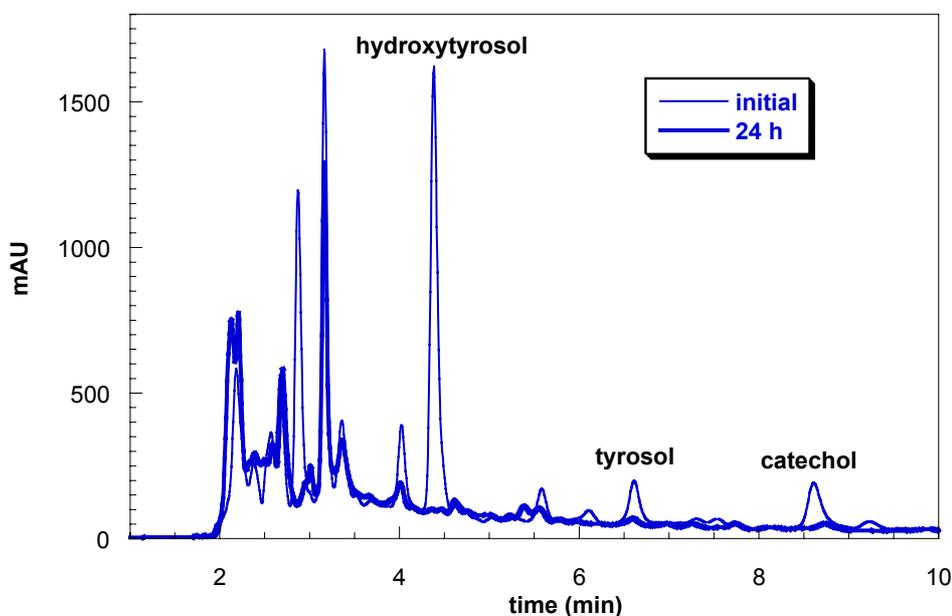


Figure 1: HPLC chromatogram of OMW before and 24h later the contact of soil

4. Conclusions

Phytotoxicity (measured by germination of *Lepidium sativum*) and microbial toxicity (tested on the growth of *Bacillus cereus*) of OMW are quite strong and a high dilution of the wastewater is needed to observe germination of the seeds or growing of bacteria.

Oxidation of pure phenolic compounds found in OMW, catechol and tyrosol, has been studied in soil slurries. Final reaction products are high molecular weight polymeric compounds whose structure is similar to that of humic and fulvic acids. The same reaction occurs when real OMW are placed into contact with the soil. Polyphenols contained in OMW are converted in 24 h in an aerated soil slurry.

The removal of phenolic compounds is bound to a slight decrease in phyto- and microbial toxicity. This suggests that other compounds in OMW are responsible of toxicity in the soil environment. Further studies will be devoted to assess the nature of these compounds in order to develop a possible treatment to reduce the damage to the soil quality when OMW are spread onto the agricultural soil.

5. Acknowledgements

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Conceptual modelling of PAH solubility in tar contaminated soil aqueous phases

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1. Introduction

The contamination of old coke oven sites is characterised by the presence of coal tar containing polycyclic aromatic hydrocarbons (PAHs) in industrial soil materials. The solubilisation of these organic pollutants in percolating water fluxes is generally limited but cannot be predicted by simplistic models based on the solubility in water and partition coefficients between water and organic matter quantified in the literature. But this solubilisation is a key process of the mobility in water and of the bioavailability for natural attenuation in soil and sub-soil media.

A lot of data is now available in the literature for the evaluation of the solubility of PAHs in pure water (S_w in mg/l) and the partition of PAHs between water and octanol (K_{ow}) (D. Mackay and al., 1992). The following table has been prepared on the basis of this data submitted to a statistical study. A log-normal distribution is the better model for characterising the present knowledge of these thermodynamical parameters. The mean of log values and the related 95 % confidence interval deviations are indicated. The uncertainty of these values is still relatively important compared to other thermodynamical data like in mineral aqueous chemistry.

Table 1 : Solubility in water (S_w in mg/l) and octanol-water partition coefficient (K_{ow}) of PAHs. Source data from D. Mackay and al. (1992). log are decimal.

PAH compounds		mean log(S_w)	95% confidence interval	mean log(K_{ow})	95% confidence interval
Benzo(ghi)perylene	BGP	-3.53	0.12	7.00	0.12
Dibenzo(a,h)anthracene	DAA	-3.04	0.35	6.61	0.21
Benzo(k)fluoranthene	BKF	-2.82	0.37	6.59	0.24
Chrysene	CHR	-2.64	0.10	5.81	0.15
Benzo(a)pyrene	BAP	-2.59	0.17	6.30	0.18
Benzo(b)fluoranthene	BBF	-2.34	0.55	6.29	0.20
Benzo(a)anthracene	BAA	-1.86	0.09	5.82	0.15
Anthracene	ANT	-1.17	0.07	4.46	0.05
Pyrene	PYR	-0.84	0.07	5.13	0.14
Fluoranthene	FLA	-0.64	0.07	5.20	0.14
Phenanthrene	PHE	0.05	0.09	4.50	0.07
Fluorene	FLE	0.30	0.06	4.22	0.05
Acenaphthene	ACE	0.53	0.16	4.04	0.10
Acenaphthylene	ACY	0.69	0.26	3.95	0.11
Naphthalene	NAP	1.50	0.05	3.40	0.06

In the case of tar contamination, PAHs are present in a complex mixture including various other hydrocarbons. This mixture can be modelled as a potentially diphasic (solid-liquid) ideal mixture system where the thermodynamical parameters of phase exchanges and individual solubilities of solid compounds in water are known.

The description of the solid and liquid tar phases is generally based on an ideal mixture model where the activity of each compounds is equal to the molar fraction. The solid-liquid transition can be described using the thermodynamical data on the melting of pure compounds (melting temperature T_m and entropy change ΔS_m). When two phases are present, the molar fractions of lower molecular weight compounds are higher in the liquid phase. In addition, the presence of liquid aromatic compounds at normal temperature, like toluene, enhances the formation of a liquid tar phase. Depending on the temperature and the nature of organic compounds, the tar can be solid, diphasic or liquid. Here we try to progress in the validation of a conceptual model allowing to describe the contact between tar and water that can occur in soil or sub-soil systems.

2. Methods

2.1 Conceptual model for the solubilisation in water

The proposed model is based on the thermodynamical description of individual phenomena involved in the solubilisation of pure solid PAHs in water : the mobile order theory (P. Ruelle and al., 1992, 1993, 1994a and 1994b). It includes, the melting of the compound, the non ideal mixing in the liquid aqueous phase and the main interactions occurring in water (unspecific solubility effect, specific hydrophobicity effect, and specific interaction between hydrogen and pi-aromatic bonds). This model gives an estimation of the logarithm of the molar fraction in water $\log(X_w)$ as a sum of five terms : $\log(X_w) = A + B + C + D + E$

The melting term (A) is calculated from the entropy of melting and the related characteristic temperature. The model is the following : $A = \Delta S_m / R (1 - T_m / T)$.

The mixing term (B) only depends on the difference between the molar volumes of PAH compounds (V_m) and water (V_w). The molar volume of water is 18 ml/mol. The following formula is used : $B = 0,5.(V_m / V_w - 1) - 0,5.Log(V_m / V_w)$.

The hydrophobicity term (C) is linked to the unfree mixing of unpolar compounds in polar liquids where the intermolecular interactions are relatively strong through hydrogen bonds. This term depends on the presence of the two hydrogen bonds of water molecules and on the molar volumes : $C = - 2 V_m / V_w$

Table 2: Values of thermodynamical parameters necessary to quantify the solubility model terms. V_m and δ_m has been estimated from QSAR calculations (R.F. Fedors, 1974). T_m and ΔS_m has been estimated from melting enthalpy and melting temperature when available in Mackay and al. (1992) or is equal to 50 for missing ΔS_m values (*).

PAH compounds		V_m (cm^3/mol)	ΔS_m ($\text{J}/\text{mol}/^\circ\text{K}$)	T_m ($^\circ\text{C}$)	δ_m ($\text{J}.\text{mol}/\text{cm}^3)^{1/2}$
Dibenzo(a,h)anthracene	DAA	252.6	57.6	268.0	21.6
Benzo(ghi)perylene	BGP	233.8	31.6	275.9	22.6
Benzo(k)fluoranthene	BKF	222.8	50.0*	213.8	22.0
Benzo(a)pyrene	BAP	222.8	38.5	176.7	22.0
Benzo(b)fluoranthene	BBF	222.8	50.0*	167.8	22.0
Chrysene	CHR	211.8	49.6	254.3	21.4
Benzo(a)anthracene	BAA	211.8	49.3	160.3	21.4
Pyrene	PYR	182	40.2	153.0	21.8
Fluoranthene	FLA	182	49.4	109.4	21.8
Anthracene	ANT	171	58.8	216.9	21.0
Phenanthrene	PHE	171	44.3	99.0	21.0
Fluorene	FLE	165.5	50.4	115.5	20.4
Acenaphthene	ACE	160	58.7	93.9	19.9
Acenaphthylene	ACY	141.2	50.0*	90.6	21.4
Naphthalene	NAP	130.2	54.0	80.8	20.3

The unspecific solubility term (D) is related to the polarity of the compounds which can be described by the solubility equation depending on the solubility parameters of the PAH compounds δ_m and water δ_w . This equation gives : $D = -V_m / (RT) \cdot (\delta_m - \delta_w)^2$

The interactions between hydrogen and pi-aromatic bonds generate a specific term (E) which is constant for every PAHs: $E = \text{Log}(1 + 80 / V_w) = 1.7$

This conceptual model allows to predict the solubility of PAHs in water using four thermodynamical parameters. Data available in the literature for PAHs are listed in the following table.

2.2 Conceptual model for the solubilisation in octanol

The same model can be used for describing the solubilisation in an octanol phase in contact with water. The molar volume of the octanol phase must be estimated. It depends on the molar volume of octanol, the molar fraction of water in the phase (ϕ_w) and the molar volume of water. Using the solubility of water in octanol, it is possible to estimate these values. The molar volume of octanol is 156.2 cm³/mol and the volumic fraction of water in octanol at normal temperature is about 5 % : the resulting mean molar volume is 112.8 cm³/mol. In addition, the solubility parameter of octanol is 16.4 (J.mol/cm³)^{1/2}.

Replacing V_w by the mean molar volume of the mixture in the model, it is possible to estimate the logarithm of the molar fraction of PAHs in the octanol phase. The term A is unchanged and the term B can be easily recalculated. In the term C, the coefficient 2 must be corrected taking into account the volume fractions of water (coefficient 2) and octanol (coefficient 1) : a coefficient 1.95 is obtained. The term D is replaced by the sum of two terms. One for the unspecific interaction with octanol, with a factor of $(1 - \phi_w)^2$ and one for the unspecific interaction with water, with a factor of ϕ_w^2 . Lastly the term E depends only on the presence of water in the phase : $\text{Log}(1 + \phi_w \cdot 80 / V_w)$.

Conceptual model for the solubilisation from liquid tar mixtures

In the case of liquid tar mixtures, the melting is done and the mixing effect can be simplified to an ideal mixing phenomena assuming similar molar volumes and no important interaction effects. The molar fraction of PAHs in water in contact with liquid tar mixtures is thus obtained replacing the term A by the molar fraction in the liquid tar.

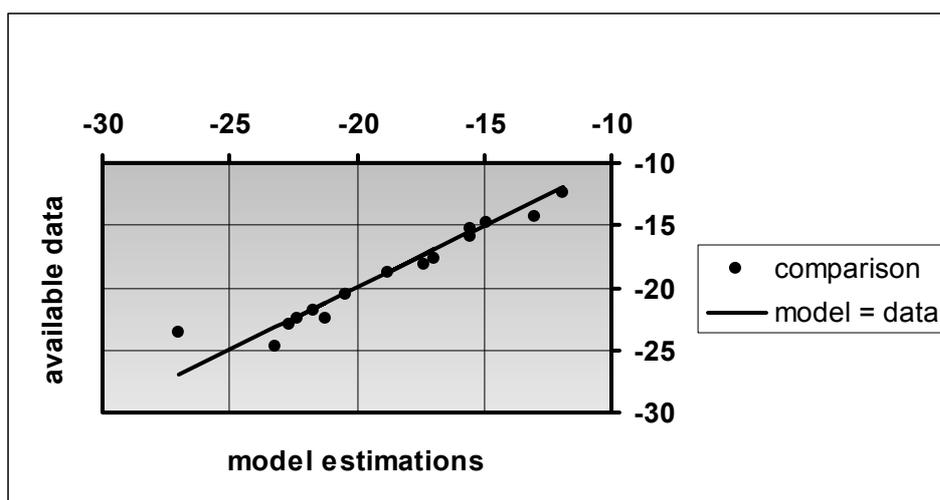


Figure 1: Comparison between $\log(X_w)$ obtained from the literature and from the selected conceptual model (X_w is the molar fraction in water at 25°C).

3. Results and Discussion

3.1 PAH solubility in water

To illustrate the validity of the conceptual model, a comparison of available data from the literature (water solubilities of PAHs in Tab. 1) with the estimations of the model is illustrated in the Fig. 1. The results are very promising for the 16 PAHs of the EPA list. Only one compound show a significant discrepancy between data and estimations : dibenzo(a,h)anthracene.

3.2 PAH partition between octanol and water

To illustrate the validity of the conceptual model in the case of an organic phase, a comparison of available data from the literature (octanol-water partition coefficients of PAHs) with the estimations of the model is illustrated in the Fig. 2. The results are also very promising for the 16 PAHs of the EPA list. A systematic error seems to appear for the highest molecular weights. The same compound show an important discrepancy between data and estimations : dibenzo(a,h)anthracene.

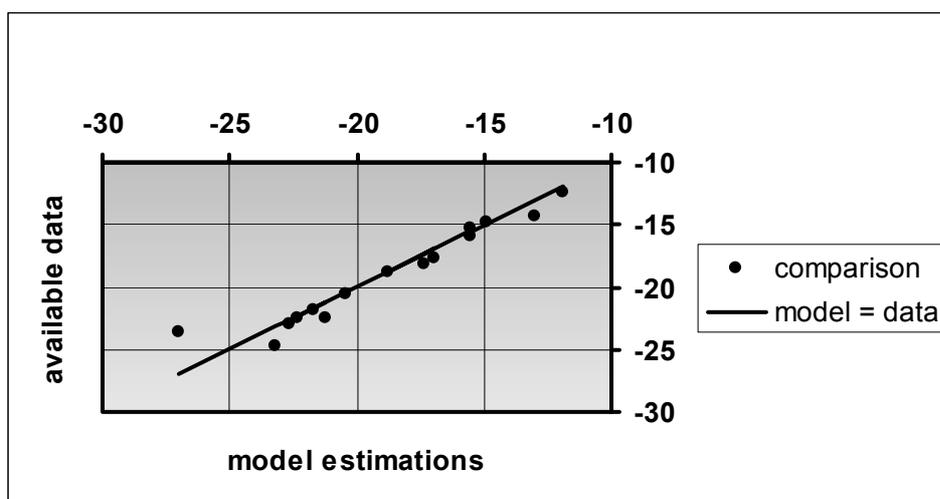


Figure 2: Comparison between $\log(X_o)$ obtained from the literature and from the selected conceptual model (X_o is the molar fraction in an octanol phase in contact with water at 25°C).

3.3 PAH solubilisation in water from a liquid tar mixture

To illustrate the validity of the conceptual model in the case of liquid tar mixture in contact with water, a comparison of available data from the literature (tar molar fraction and related water concentration for four different tars listed in Tab. 3) with the estimations of the model is illustrated in the Fig. 3. The estimation is very good for all the compounds and for the four situations.

Table 3: experimental tar molar fractions and related observed water concentrations for four artificial tar containing PAHs and toluene. Source data from C. Peters and al. (1997).

PAH compounds	X_{tar}	$\log(C_w)$	X_{tar}	$\log(C_w)$	X_{tar}	$\log(C_w)$	X_{tar}	$\log(C_w)$
Pyrene	0.074	0.08	0.044	0.11	0.058	0.07	0.051	0.07
Fluoranthene	0.153	0.21	0.091	0.24	0.117	0.16	0.104	0.16
Phenanthrene	0.175	0.73	0.104	0.58	0.135	0.57	0.119	0.50
Fluorene	0.087	1.01	0.053	0.66	0.067	0.76	0.060	0.67
Acenaphtene	0.203	3.50	0.121	2.10	0.155	2.50	0.137	2.24
2-ethylnaphtalène	0.094	0.85	0.056	0.51	0.146	1.23	0.129	1.07
1-methylnaphtalene	0.214	6.90	0.233	7.30	0.301	9.20	0.266	8.00
Naphthalene	-	-	0.297	29.40	-	-	0.116	11.30
Toluène	$3.9 \cdot 10^{-6}$	0.08	$3.9 \cdot 10^{-6}$	0.11	0.021	10.70	0.018	8.00

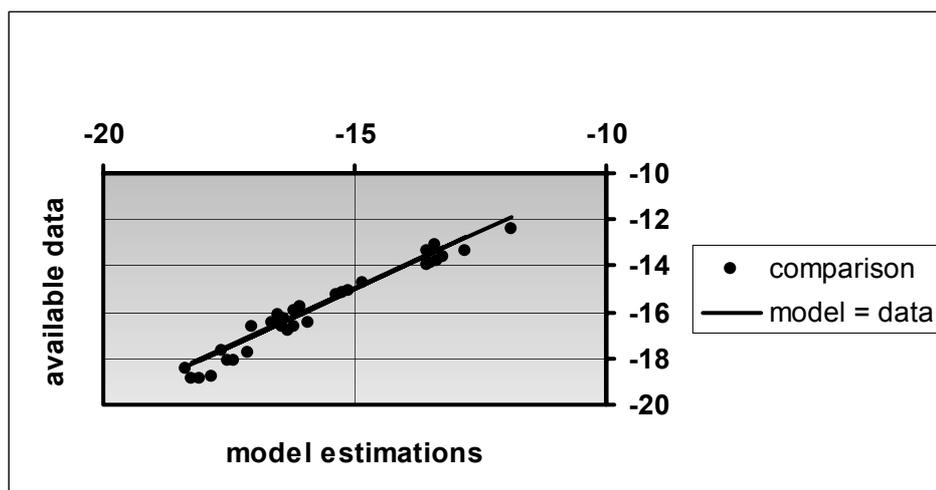


Figure 3: Comparison between $\log(X_w)$ obtained from the literature and from the selected conceptual model (X_w is the molar fraction in water at 25°C).

4. Discussions and perspectives

This concept allows to predict changes in water apparent solubilities of individual compounds with temperature and molar fractions of each compounds in the tar mixture. This approach is partially validated through the comparison of data available in the literature with model estimations. In addition to these changes of the chemical activity of compounds in the tar system, the aqueous soil solution can be modified by the presence of organic and ionic solutes. Generally, the presence of ionic compounds limits the solubility of hydrophobic substances and the presence of soluble hydrocarbons increases it. The proposed thermodynamical approach can be used for studying and predicting these phenomena. It allows to propose a similar approach for the characterisation of the non ideal PAHs distribution between tar and aqueous phases in coal tar contaminated industrial soils. In the future, this type of model will be included in existing solute transport models as ion non ideal behaviour has been done before.

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Environmental and agronomic problems associated with long term effects of irrigation with reclaimed wastewater

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Abstract: Irrigation with reclaimed wastewater (RW) becomes common, particularly, in regions where it is a prerequisite for the continuation of agricultural production and sustainable development. Apart of economizing and increasing use efficiency of water, it offers the potential of recycling plant nutrients (N, P, K). While increased salinity and boron levels, presence of pathogens, accumulation of heavy metals and deterioration of soil structure are recognized as potential threats associated with RW, little attention was given so far to environmental and agronomic problems associated with N and P in the RW. The adverse environmental effects of irrigation with RW particularly when relatively high BOD, bicarbonate and pH levels coincide with management difficulties of N and P supply (inherent for RW for irrigation) are addressed. These often lead to: reduced N use efficiency and N recovery; accumulation of nitrate in soil profile and/or its enhanced leaching to ground water; formation of toxic levels of nitrite near soil surface; increased gaseous losses due to denitrification, raised emission rates of N₂O (due to both nitrification and de-nitrification) and higher NH₃ volatilization. Phosphorus accumulation in soils irrigated with RW reached alarming levels threatening both water sources (e.g., due to surface contamination by runoff) and the availability of micronutrients in soil (e.g., Zn). The mechanisms and processes associated with the above mentioned problems are examined focusing on Mediterranean-like and semi arid soils and key factors essential for a safer utilization of RW in agriculture are discussed.

1. Background

The use of reclaimed wastewater, RW, for irrigation is an important alternative for disposing this waste, particularly in arid and semiarid areas where it can alleviate the problem of water shortage. Effluent irrigation plays an important role in Israel, where currently it contributes more than 30% of the water used for irrigation and it is expected to contribute more than 50% within the next 10 years.

A large part of the RW used for irrigation contains significant quantities of macronutrients, especially N, K and P. The average concentrations of total N and P (organic and mineral) in RW used for irrigation of citrus in Israel are about 25-30 mg N l⁻¹ and 6-7 mg P l⁻¹ whereas the concentrations of the mineral forms are 19-23 mg N l⁻¹ and 3-4 mg P l⁻¹, respectively (Tarchitzky et al., 2004). Nitrate concentration in effluents is usually below 1-2 mg N l⁻¹. Management of nutrient supply is inherently problematic with RW due to the fact that the nutrients in the RW are continuously supplied whenever irrigation is applied regardless of plant requirements and for some crops, N and P added via the RW, exceed the amount commonly applied via common irrigation with fresh water.

Since N and P in the RW are present in inorganic and organic forms there is a need to account for soil transformations of both. Most of the studies dealing with RW have concentrated on the transformations of mineral forms (Feigin et al., 1981; Zhou et al., 2003). There is limited knowledge regarding the dynamics of organic N and P in RW irrigated soils and regarding the influence of factors such as BOD, Eh, pH, bi-carbonate and total C on the transformations of these nutrients as well as the long-term environmental and agronomic effects resulting from use of the RW. The required information is very important for improving irrigation management with secondary and in some case even tertiary RW containing relatively high levels of N and P. Farmers expecting the nutrients in RW to further economize its use may face agronomic problems and inflict environmental damage due inherent management problems associated with difficulties to synchronize nutrient supply with plant demand and the un-desired interactions of the nutrients with other RW constituents (e.g., BOD levels

of 10-30 mg l⁻¹, increased pH levels).

Efforts were made in Israel in the last decade to monitor and better understand the long-term effects associated with RW irrigation by encouraging laboratory, lysimeter and field research and by initiating in 1998 the “National Wastewater Effluent Irrigation Survey” (e.g., Tarchitzky et al., 2004), covering more than 150 citrus orchards out of which 80% are irrigated with RW.

This presentation summarizes main finding related to N transformations and N and P dynamics and long-term effects associated with the use of RW on agricultural land.

2. Nitrogen Transformations in RW Irrigated Soils

2.1 Gaseous N losses from RW irrigated soils

Using labeled ¹⁵N-NH₄ and ¹⁵N-NO₃, (Master, 2002) has shown that irrigation with secondary RW induced higher rates of N₂O emission from lysimeters packed with a sandy loam on which maize was grown. In incubation studies with a calcareous clay irrigated with RW the effluent doubled the rates of N₂O emission as compared to irrigation with fresh water (Master et al., 2004). Interestingly, a significant proportion of the formed N₂O was via nitrification (Master et al., 2003, 2004). Ammonia volatilization from the surface of RW irrigated soils was almost doubled as compared to fresh water (Master, 2002, Master et al., 2003) and yet the total losses of NH₃ and N₂O were assumed to be underestimated due to experimental conditions. Losses of N₂ due to denitrification in the surface layer of a calcareous clay were expectedly negligible. The losses determined for the surface soil layer under saturation (laboratory incubations) reached ~4% of the applied N and were twice higher with the RW as compared to fresh water. The loss of N₂ from deeper (anoxic) soil layers was not determined but was expected to be significantly larger and particularly with RW in which nitrate and organic compounds (electron donors, BOD) are supplied in excess.

The higher pH levels in the RW were assumed to be a major driving force for the increased NH₃ losses and may also increase the solubility of OM and thus indirectly affect the processes sensitive to oxygen depletion.

2.2 Nitrification and mineralization rates in RW irrigated soils

Master et al. (2004) showed that the average gross nitrification rates, estimated via isotopic dilution, were 11.3 and 15.8 mg N kg⁻¹ d⁻¹ for a fresh water and RW irrigated calcareous clay, respectively. Average gross mineralization rate estimates were about 3 mg N kg⁻¹ d⁻¹ for both fresh water and RW irrigated soils. Oved et al. (2001) found that the predominant population of ammonia oxidizing bacteria changed from *Nitrosospira* in fresh water irrigated soils to *Nitrosomonas* in soils exposed to RW irrigation. Yet it is not clear to what extent such changes affected the observed changes in rates of nitrification.

Zhou et al. (2003) determined first order rate constants for the “net” mineralization of RW-originated organic N in: a sandy loam, a loess soil and a calcareous clay to be 0.3 week⁻¹, 0.4 week⁻¹, and 1.1 week⁻¹, respectively. This practically implies that the organic N originating from a secondary RW is likely to be mineralized in 3 representative Mediterranean soils within 1 to 3 weeks after its application. Zhou et al. (2003) also found that the organic N movement in soil columns was faster than that of NH₄ implying that the mineralization of the organic N originated in the RW may also occur in deeper soil layers and not only in the surface layer. This could provide an additional explanation to the lower levels of N recovery observed with RW irrigated soils in lysimeters (Shaviv et al., 2003).

2.3 Nitrite formation

Master et al. (2004) and Shaviv et al. (2003) found a five to tenfold increase in nitrite levels formed in RW irrigated soils as compared to fresh water irrigated one. The most prominent effect was observed when re-wetting (or re-irrigating) the soil after a drying period of a few days. Daily irrigation with RW resulted in nitrite levels of 1-3 mg N l⁻¹ whereas irrigation once in 4 days induced nitrite formation of 10-20 mg N l⁻¹. The higher levels may be toxic to many crops and thus special attention should be taken when using RW to avoid nitrite accumulation. The higher rates of nitrite formation in RW

irrigated soil were attributed to the increased pH (about 0.5 units higher than in fresh water), raising NH_3 volatilization rates thus reducing the activity of *nitrobacter* and allowing the temporary accumulation of nitrite 1 – 2 days after irrigation. Noteworthy is the fact that ammonium applied in fresh water to a soil with a long history of RW irrigation induced high nitrite levels similar to those caused by irrigation with RW containing high BOD, implying that the long-term exposure of the soil to RW dominated this processes.

3. Nitrogen balance and agronomic aspects in RW irrigated soils

3.1 Results of a long-term lysimeter experiment

Based on N budgets, Shaviv et al. (2003) showed that the N recovery in RW irrigated maize, grown in lysimeters packed with 3 representative soils, was 20-30% lower than in fresh water irrigated ones. Estimates of gaseous losses performed by Master et al (2003, 2004) for the same soils could account only for about 5% of the differences, but these were assumably underestimated due to the experimental conditions. Emission of NO (nitric oxide) was not measured in these experiments, and it is suspected that losses via formation of this gas could be large in soils supplied with high levels of OM particularly when applying an NH_4 source to a relatively dry soil surface (e.g., Drury et al., 1992; Hutchinson et al., 1993). Some of the un-recovered N could be attributed to increased N losses due to leaching of the organic N fraction from RW irrigated soils.

Nitrate leaching from the RW irrigated lysimeters was only slightly higher and generally non-significant in comparison to fresh water. This result was expected since the N supply with the two irrigation treatments was similar.

The yields obtained during 6 years of the experiment were about 10% lower for the RW irrigated sandy loam and calcareous clay and only slightly affected in the loess soil. The yield reduction could be due higher salinity and/or boron levels in the RW irrigated soils or to increased levels of nitrite temporarily formed in RW soils when intervals between irrigation events were larger than 3 days.

3.2 National wastewater effluent irrigation survey

More than 150 plots in commercially operated citrus orchards were extensively surveyed since 1998 providing detailed information about of the supplied amount of water, and inputs of salinity (EC, SAR), boron, dissolved organic matter (BOD), nutrients (N, P, K) and trace/transition elements (e.g., Tarchitzky et al., 2004) contained in the water. Extensive soil sampling at 4 depths (0-120 cm) and leave tests were performed twice a year in March (beginning of the spring, before irrigation with RW started) and October (end of irrigation with RW).

One of the most striking findings in the survey is fact that farmers apply double amounts of N with the RW as compared to irrigation with fresh water (470 (46) kg-N ha^{-1} and 245 (25) kg-N ha^{-1} , respectively). This happened despite the recommendation to account for the N in the RW and apply an excess of about 30% N as compared to the common practice to compensate for potential losses. The surplus N in the RW irrigated soils was reflected in the levels of N in soil profiles being about 40 - 50% higher in the RW soils. Moreover, the levels of N in the 120 cm soil profiles at the beginning of the autumn, when the uptake by the trees slows down, exceeded the estimated N removal in the harvested fruits. The amounts of N detected in soil profiles in the following spring were reduced due to leaching and gaseous losses but were still comparable with the estimated N removal in fruits. Rough estimates indicate that the “net” losses of N during the winter were larger in the RW plots.

Based on estimates of N removal in the harvested fruits and N inputs, N-use efficiencies (NUE) of ~ 20% and ~ 40% were obtained for the RW and fresh water irrigation, respectively.

4. Phosphorus dynamics in columns, lysimeters and citrus soils

4.1 Column and lysimeter experiments

In a column experiment with a sandy loam and a loess in which ryegrass was irrigated with secondary RW and fresh water, Goldrath (2001) found P leaching losses of 5% and 2.5% in the drainage of the RW and fresh water irrigated columns, respectively. The leaching from the loess soil was similar for the two types of water amounting only to 0.5% of the applied P. The pH determined in the upper soil layer (~ 5cm) of the sandy loam was ~ 6.5 and 8.0 for the RW and fresh water, respectively. The pH's for the same depth in the loess soil were ~ 7.7 and 8.3, respectively. Calcium and magnesium concentration in the drainage of the RW were about 10 - 20% lower as compared to the fresh water. Considering also the higher levels of dissolved OM (i.e., BOD) in the RW, a "net" reduction in Ca and Mg activities in soil solution and thus an increase of P availability, particularly in the lighter soil, should be expected. Similar although less prominent trends were observed for P in the lysimeter experiment.

4.2 National wastewater effluent irrigation survey

Based on the assumption that P is likely to be easily fixed in the semi-arid soils of Israel efforts to remove this nutrient from the RW were limited and thus the levels of 6 -7 mg P l⁻¹ in the RW used for irrigation (Tarchitzky et al., 2004) are not surprising. Excess P in the RW led to more than double supply of P via this source as compared to irrigating with fresh water. In addition, the higher pH and BOD levels and the potential reduction in Ca and Mg activity in RW irrigated soils is expected to further increase P availability. Indeed, findings obtained since 1998 (e.g., Tarchitzky et al., 2004) clearly indicated a very significant increase of bicarbonate-extracted P ("Olsen Method") from an average of 10 – 20 mg P kg⁻¹ in the top layers of fresh water irrigated soils to 35 – 55 mg P kg⁻¹ in top layers of RW irrigated soils. The effects were more prominent with the lighter soils, with drip irrigation as compared to sprinkler irrigation, and with the increase in the duration of soil exposure to RW. In sandy loam soils, drip irrigated with RW for 15 – 20 years the levels of Olsen P in top layers reached 75 mg P kg⁻¹. With sprinkler irrigation of RW under similar conditions the values were 35 – 40 mg P kg⁻¹ and with fresh water only 10 –12 mg P kg⁻¹. Levels of 20 –25 mg P kg⁻¹ were detected at the depth of 120 cm in the lighter soils (i.e. clay below 20-30%) exposed to RW, while in the heavier soils (i.e. clay content above 30%) it reached ~ 5 mg P kg⁻¹ regardless of the water source.

From the agronomic point of view, P availability in most of the RW irrigated plots can be defined as "excess P" suggesting that P may not be needed to sustain the citrus growth in the near future. Moreover, too high levels of available P are likely to induce deficiencies of micronutrients like Zn, in the some of the tested soils.

From the environmental point of view the increasing levels of mobile P at soil surface may increase the threat of P removal via runoff from the agricultural land to adjacent water sources. When adding to this the potential of increased runoff from RW irrigated soils (due to higher SAR values) the P pollution damage may be even greater.

5. Conclusions

The results obtained for both N and P dynamics in RW irrigated soils provide a clear picture of management problems associated with supply of the nutrients via RW leading to over dosing and inflicting environmental and even agronomic damage.

The basic problem stems from the inherent contradiction between the desire to economize nutrient use and the fact that their supply via RW in most cases cannot be synchronized with plant demand. In addition, fertigation management when using RW faced also difficulties due to knowledge gaps regarding possible changes in mechanisms and reaction rates caused by the RW. These include processes such as: nitrification, denitrification, mineralization, nitrite formation, nitrous oxide formation and P transformations found to be affected by the RW and particularly in soils exposed to it for longer periods.

The contradiction between farmers demand to retain high N and P levels in the RW on the one hand and the fact that they merely accounted for the surplus of these nutrients in RW on the other cannot be ignored; particularly in the light that the poorly managed application of these nutrients induces severe environmental damage and agronomic problems. These are part of the dilemmas standing currently in the center of a debate in which water specialists, agronomists, environmentalists and decision makers are involved trying to figure out the best policy and practices for a safer utilization of RW in a region where water shortage must be overcome in one way or another.

In the meanwhile, the findings of the last 5-6 years are utilized to re-structure the recommendations given to farmers to improve the management of RW application in general as well as that of N and P supply. At the same time efforts are done to impose better control of the quality of the RW produced for irrigation and to introduce stricter regulations in a manner that will assure utilization of higher quality RW by all its end users.

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**SESSION III:
HETEROGENEITY AND SCALE ISSUES
IN SOIL AND GROUNDWATER**

KEY NOTE: Flow and transport at basin scales: new tools, open problems

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1. Introduction

The lecture summarizes recent and established results from Lagrangian theories of transport, which are deemed appropriate to describe natural transport processes at large (e.g. basin) scales - indeed relevant to nonpoint source transport. In particular, emphasis is placed on the hierarchical derivation of transport properties, from the features of conservative matter, described by travel time distributions of the carrier flow in the important case of decoupled flow and transport properties, to the derived features of solute lifetime distributions embedding the net effects of physical, chemical and biological reactions. In particular, the lecture focuses on:

- geomorphological theories of the hydrologic response, the best suited approaches, in the writers' opinion, to tackle large-scale transport problems. These approaches define the statistical features of the carrier flow through travel time distributions, and fully embed, in a stochastic framework, the potentially heterogeneous features of natural media interested by the transport phenomena;
- the derivation of lifetime distributions of matter carried by hydrologic flows. Because the engine for mass exchange between fixed and mobile phases is the contact time, easily assimilated to travel time (were independent decays negligible), a suitable exact framework can be established in a few cases, namely: i) the case of well-mixed hydrologic states (i.e. the case where resident and fixed-phase concentrations can be assumed as simply time-dependent) (Rinaldo and Marani, 1987; Rinaldo et al., 1989); and ii) the case of steady carrier flow (Dagan & Cvetkovic, 1994) which resulted in noteworthy applications (Gupta and Cvetkovic, 2000; Simic and Destouni, 1999; Lindgren et al., 2004).

Here we discuss merits and disadvantages of the two approaches, jointly with their likely capability of describing cases of practical interest with reference to NPSP transport in general and specifically to a case study. We shall also discuss how we plan to inch towards a general solution, still awaiting its establishment, possibly capable of relaxing the limitations of both existing approaches.

2. Theoretical framework

Given the heterogeneity of the processes involved, as well as the intrinsic variability of the physical and chemical features of the natural environment where the hydrological transport take place, the stochastic models are commonly adopted in transport modeling at basin scale. Following the probabilistic framework, we admit that a particle moving within the control volume and driven by the hydrologic carrier flow has a trajectory which, at time $t > 0$, is only partially known, i.e. through its probability distribution in space and time. Let thus $m(\mathbf{X}, t; \mathbf{a}, t_0)$ be the mass, evaluated at time t , of (or transported by) a water particle injected at time t_0 in the (arbitrary) initial position $\mathbf{X}(t_0) = \mathbf{a}$. Each

trajectory is defined by its Lagrangian coordinate $\mathbf{X}(t) = \mathbf{X}(t; \mathbf{a}, t_0) = \mathbf{a} + \int_{t_0}^t \mathbf{u}(\mathbf{X}(\tau), \tau) d\tau$ where $\mathbf{u}(\mathbf{X}, t)$

is the lagrangian velocity vector. The initial mass $m(\mathbf{x}_0, t_0)$ of the water particle injected may or may not change with time and/or space depending on the presence of (non conservative) mass-exchange phenomena.

2.1 Transport of passive scalars and geomorphologic theories

The flux of the carrier is commonly seen as a conservative process: the water particles injected are thought as unities moving within the control volume towards the outlet without significant variations of their mass ($m(\mathbf{x}, t) = m$). In this case, the spatial distribution of mass concentration in the (arbitrary) volume V as a result of the injection of a single particle is thus given by (Taylor, 1921): $C(\mathbf{x}, t) = m\delta(\mathbf{x} - \mathbf{X}_t)$, where $\delta(\cdot)$ is Dirac's delta distribution, $\int_V (C/\theta) d\mathbf{x} = m$ and θ is the possibly existing 'porosity' of the transport volume, i.e. the coefficient defining the active portion of the transport volume. In the one-particle world, concentration (mass per unit transport volume) is thus nonzero only at the site where the particle is instantaneously residing (i.e. at its trajectory). The evolution in time and space of the trajectory of the particle is defined by the heterogeneity of the underlying hydrological processes and is therefore seen as a random function. Let $g(\mathbf{X}) d\mathbf{X}$ be the probability that the particle is in $(\mathbf{X}-d\mathbf{X}), (\mathbf{X}+d\mathbf{X})$ at time t . The uncertainty cast on the particle's position in time and space is related to the difficulty in characterizing completely the complex chain of events making up hydrologic transport processes (and, in particular, rainfall-runoff generation processes). Convection processes of interest in this context are, in fact, strictly related to hydrologic transport phenomena and, as such, they are affected by the natural heterogeneity of the media at basin-scale. The ensemble average (i.e. many realizations) concentration $\langle C(\mathbf{x}, t) \rangle$ over all possible paths is then given by the classic relation (Taylor, 1921; Dagan, 1989): $\langle C(\mathbf{x}, t) \rangle = m g(\mathbf{x}, t)$. By integration of the ensemble mean of the concentration $\langle C \rangle$ over the control volume V one gets the mass stored within the control volume $\langle M(t) \rangle$ and therefore, by derivation, the mass flux $Q(t)$ exiting the system from the absorbing barrier:

$$Q(t) = -\frac{d \langle M(t) \rangle}{dt} = -\frac{d}{dt} \int_V \langle C \rangle d\mathbf{x} \propto -\frac{d}{dt} P[T \geq t] = f(t) \quad (1)$$

In equation (1), $P[T > t]$ is the cumulative probability for the residence time within the control volume and its temporal derivative $f(t)$ is the probability density function for the basin residence time. The catchment response may be thus modelled embedding all the sources of uncertainty within the travel time distribution $f(t)$, which represents the underlying instantaneous unit hydrograph. The determination of the catchment travel time distribution $f(t)$ is based on the network geometry and may be obtained collecting all the contributions of the different paths Γ to the basin outlet:

$$f(t) = \sum_{\gamma \in \Gamma} p(\gamma, t) f_{x_\omega} * \dots * f_{x_\Omega}(t) = \sum_{\gamma \in \Gamma} p(\gamma, t) f_\gamma(t) \quad (2)$$

The specification of the path probabilities $p(\gamma, t)$ in Eq. (1) is allowed by the reconstruction of the space and time distribution of the rainfall fields, which may be in turn obtained by a suitable geostatistic interpolation procedure (e.g. through kriging techniques). In this context, the total discharge $Q(t)$ at the outlet of the basin may be expressed in a convolutive form:

$$Q(t) = \sum_{\gamma \in \Gamma} \int_0^t p(\gamma, t') j(t') f_\gamma(t - t') dt' \quad (3)$$

Note also that the expression given in Equation (3) may also account for the effects due to the runoff formation processes, as well as the intrinsic variability of the hydrologic properties of the soils depending on the actual land use.

2.2 Transport of reactive solutes & mass response functions

If we admit that, owing to the chemical exchange between the carrier and other fixed phases (e.g. chemical or physical sorption, ion exchange, precipitation) the mass transported by the moving

particles may vary both in time and in space, the general problem may be solved by neglecting the temporal dependence of the velocity field (i.e. $\mathbf{u}=\mathbf{u}(x,y,z)$). Under the steady flow assumption the Lagrangian transport equation, which defines the evolution of the concentration C along a single streamline, is in fact (Cvetkovic and Dagan, 1994):

$$\frac{\partial C}{\partial t} + \frac{\partial C}{\partial \tau} = R \quad (4)$$

In equation (4) R is the sink/source term due to the reaction processes involved while the Lagrangian variable $\tau=\tau(x;t_0,\mathbf{a})$ represents the time that the particle injected in the control volume takes to reach a control plane orthogonal to the mean flow direction located in x and is therefore defined by the implicit relationship $X(t)(t;t_0,\mathbf{a})=x$ (where $X(t)$ is the component of the trajectory along the mean flow direction). Here we shall not review the mathematical development of solute lifetime distributions derived in the above case of steady carrier flows (Dagan & Cvetkovic, 1994). It can be shown (Botter et al., 2004) however that a special case of the transport equation can be derived in the important case $C(\tau,t) \sim C(t)$ (i.e. the case where mobile phases are well mixed thereby dependent only on the contact time and not on the position). The mass response function (i.e. the mass discharge corresponding to an instantaneous unit water release) $G(t)$ ($[T]^{-1}$) links the hillslope mass discharge $Q_m(t)$ ($[M][T]^{-1}$) to the rainfall input $j(t)$ ($[L]^3[T]^{-1}$) following the linear relationship (Rinaldo and Marani, 1987):

$$= \int G(t-t',t')dt' \quad (5)$$

In equation (5) t' indicates the injection time, while t is the current time. The difference $t-t'$ thus represents the contact time between the phases (the time available for the reaction process, which is a random function due to the heterogeneity of the transport). The mass response function G may be expressed by the product between the transfer function of the carrier (i.e. the carrier travel time distribution $f(t)$) and the water solute concentration C^* , defined as the ratio between the mass of solute and the water volume instantaneously stored within the system: $G(t-t',t')=C^*(t-t',t')f(t-t')$. The closure of the problem is ensured by a constitutive equation for the solute concentration C^* (Rinaldo & Marani, 1987):

$$\frac{\partial C(t-t',t')}{\partial (t-t')} = H \left[\frac{N(t)}{k_D} - C(t-t',t') \right] \quad (6)$$

In equation (6) H ($[T]^{-1}$) is the sorption rate between the mobile and the fixed phase, $t-t'$ represents the time available for the reaction processes for a pulse injected at $t=t'$, N is the solute concentration sorbed in the fixed phase ($[M][M]^{-1}$) and k_D ($[L]^3[M]^{-1}$) is a partition coefficient for the sorbed mass.



Figure 1: Representation of the geometric structure of the test catchment.

3. Results and discussion

The test catchment considered is the Dese-Zero river basin, a flat basin of 9000 ha draining into the Venice Lagoon. The catchment has a complex geometric structure, and is made up of four interconnected basins (Dese, Peseggia, Bazzera, Pianton) linked together through a series of tidally affected reaches (see Fig. 1). Since both discharges

and nitrate concentrations measurements are affected by the tidal fluctuations, the description of the system response required the coupling of two transport models: a geomorphological-based catchment model in order to evaluate the nitrogen loss and the discharges from the four sub-basins, and a subsequent one-dimensional propagation model accounting for convection and dispersion processes

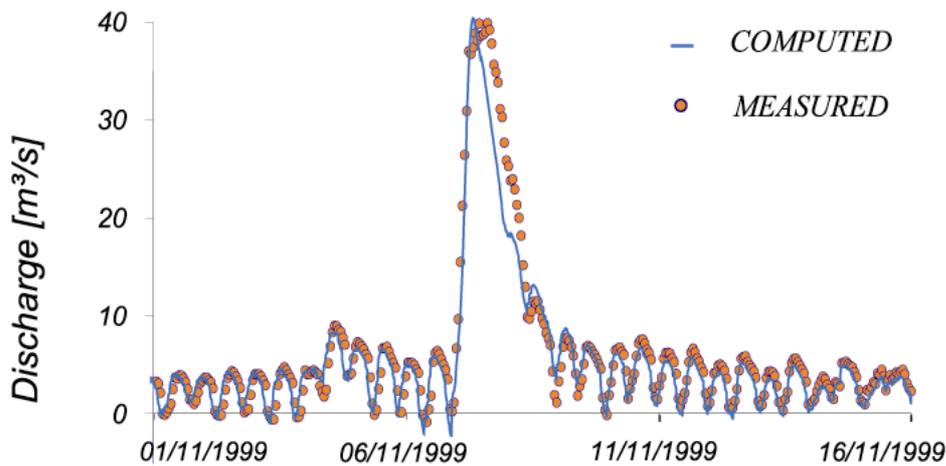


Figure 2: Flow model validation for the event of November, 1999.

occurring within the reaches which are influenced by the tidal fluctuations. The application of a

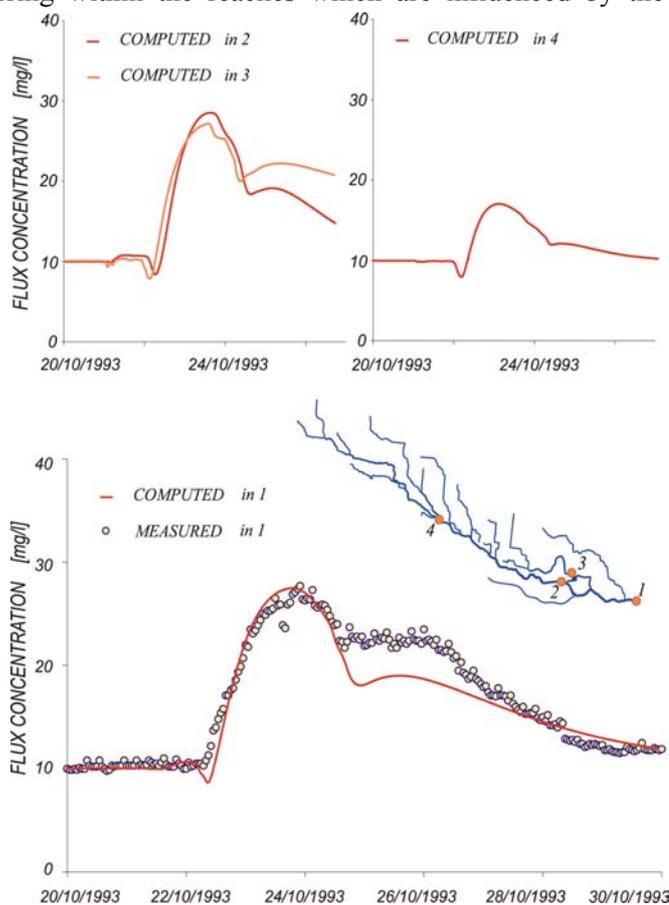


Figure 3: Model calibration: measured and computed nitrate flux concentrations at different location for the event of October 1993.

continuous geomorphologic flow model to the basins of Fig. 1, coupled with an hydraulic unsteady propagation model derived by the integration of the De St.Venant equation provided a good agreement between the modeled and the measured discharges at the outlet of the system, both during the intense rainfall events (see Fig. 2) and within the dry periods. Notice also that the coupling between a long-term macroscopic water mass balance and the geomorphologic flow model allows to reproduce the temporal variability of the soil moisture and of the evapotranspirative fluxes during a long period of time, providing a linkage between the conditions of the soil before each event to the pertinent antecedent precipitation volume. When sorption processes between the mobile and the fixed phases are super imposed to the carrier hydrologic flow, the detailed knowledge of the travel time distribution within the geomorphic states of the basin can be exploited in order to get the pertinent solute lifetime distributions for the reactive species, as described in the Section 2.2. The complete transport model

has been therefore applied during two rainfall events, respectively in October and November, 1993. This required the specification of the initial mass stored within the basin surfaces (i.e. the initial equilibrium concentration for each subbasin). To this aim a suitable soil coverage thematic map of the basin has been employed in order to evaluate the relative fraction of the basin surfaces given to agriculture use. We calibrate the model during the event of October 1993: Fig. 3 shows the resulting computed and measured flux concentrations at the outlet (bottom sketch), as well as the simulated flux concentrations at Scorzè (a node within the Dese river network, upper right sketch) and at the outlets of the Dese and of the Peseggia basins (upper left sketch). In spite of the high complexity of the processes modeled one may notice a good agreement between the computed and measured nitrates concentrations at the outlet of the basin, showing some robustness and flexibility. We also relaxed the assumption of uniformly distributed rainfall and we compute a space distributed rainfall field through geostatistics techniques (i.e. kriging). The effects of the rainfall patterns on the computed nitrogen flux concentration at the outlet have been thus investigated for the event of October 1993, as shown in Fig. 4. The major effect is produced on the tail of the hydrograph and thus on the flux concentration after five days from the beginning of the event. From Fig. 4 one may notice how the use of a spatially variable rainfall field

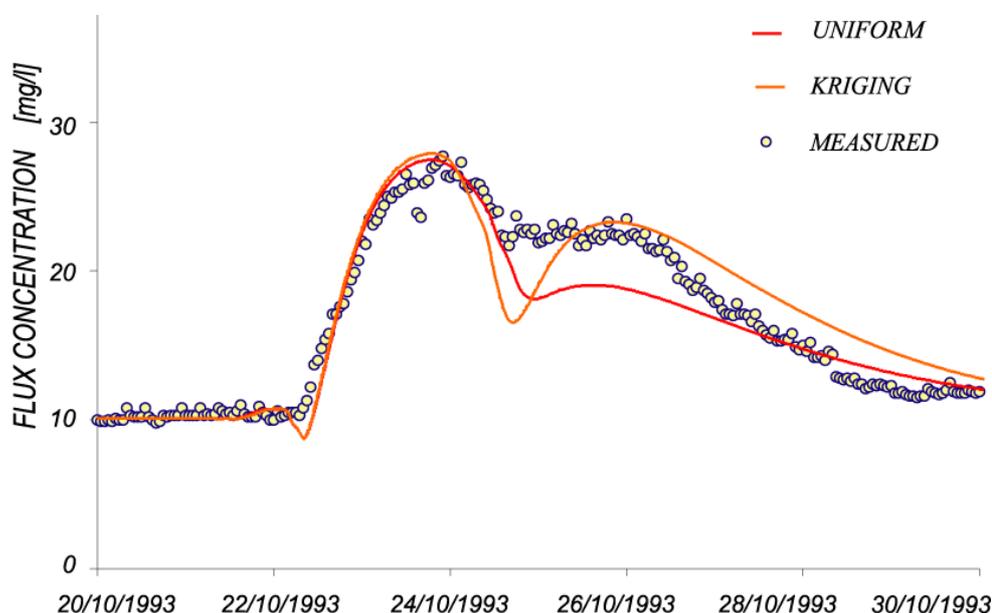


Figure 4: Effect of the spatial distribution of the rainfall for the event of October, 1999

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Upscaling biogeochemically reactive chemical transport in natural porous media

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Abstract: Aim of this research was to assess some recent advances and remaining unsolved issues regarding the effect of heterogeneity on larger scale transport for solutes that are subject to nonlinear biogeochemical interactions with the solid matrix of soil and ground water formations. Emphasis is given to research in which the porous medium is assumed to be randomly spatially variable. Two main approaches concern the resulting statistics of arrival time of solute flux and of spatial moments of solute mass. It can be established that for nonlinear interactions, transversal dispersion play a key role and that it is yet unresolved how the large scale mass balance equations should be formulated.

1. Introduction

Solute transport in natural porous formations, such as soil and geologic strata that are water saturated (e.g. aquifers), is of importance for our anticipation of the fate of natural chemicals, nutrients, pesticides, and contaminants. An essential ingredient of studying solute transport is modeling, because experimental research is time and labour intensive, limited with regard to its generality, and sometimes undesirable with regard to the integrity of our resources.

In modelling, we have to recognise that we deal with different scales. These scales are those of discretisation, of the system at hand, and the scale of the involved processes. Because these scales differ, we have to make assumptions such as that the process scale is dealt with appropriately with regard to the scale of discretisation.

In transport modeling in porous media, commonly the mass balance equation is represented by the Convection Dispersion Equation (CDE). The CDE describes transport of solutes in a continuum that replaces the actual medium that contains both a pore system and a solid phase. Therefore, the artificial construct of the continuum has to be parameterised with hydraulic functions (hydraulic conductivity and retention functions), a porosity, bulk density, and dispersivity. If the CDE is solved numerically, the continuum properties within each discretised unit cell are assumed to be constant and smeared out over the cell. Hence, the actual pore network is being replaced by a continuum that is assumed to have the same transport properties.

In the past decade, many advances have been made with regard to transport modeling for media that are characterised by random autocorrelated properties, such as hydraulic conductivity and sorption properties. Two major approaches have been followed. In the stochastic advective approach of Cvetkovic and Dagan (1996) and Destouni and Cvetkovic (1991), the travel time statistics to a control plane have been related with the statistics of the random properties, assuming that the flow domain may be visualised as an ensemble of noninteracting stream tubes. Hence, dispersive fluxes between stream tubes are ignored in this approach. This approach has been applied to a broad range of chemical interactions such as linear, equilibrium and nonequilibrium, and nonlinear sorption. This approach has been applied also to coupled unsaturated-saturated systems (Destouni and Graham, 1995) and catchments (Lindgren et al., 2004).

A related approach described the transport of solute in a random medium to arrive at the spatial statistics of solute mass distribution (Dagan, 1989). Analytical results have been obtained for the same type of problems as the stochastic advective approach (Bellin et al., 1993, Bosma et al., 1996). In these studies, local mixing is explicitly taken into account.

In the past years, these stochastic approaches to solute transport have been used to understand the displacement of solutes that undergo nonlinear biodegradation, with the aim of understanding bioremediation. Emphasis was given to the effect of heterogeneity on performance indicators such as substrate removal rate, and cleanup efficiency (Xin and Zhang, 1998, Kaluarachchi et al., 2000). It has been shown that for Monod biodegradation kinetics that involve a resident contaminant and an injected reactant, the local transport behavior may develop to traveling wave (TW) displacement (Keijzer et al., 2000). At the larger scale, it has been suggested that both TW displacement and more complex oscillating displacement may result (Oya and Valocchi, 1998).

2. Biodegradation Modeling

Recently, transport has been studied for solutes that are being degraded according to nonlinear Monod kinetics (Janssen et al., 2004) for a porous medium that is characterised by a random autocorrelated hydraulic conductivity. They made a comparison of the transport taking pore scale dispersion into account. With their initial numerical modeling using the code of Keijzer et al. (2000), to compare with the stochastic advective analytical solution of Keijzer (2000) that excludes pore scale dispersion, it appeared that only a poor agreement was obtained. The discrepancies were attributed to the overestimation of transversal solute dispersive fluxes. To reduce these fluxes required very fine discretization and excessive computational efforts.

In a second approach, the code of Cirpka and Kitanidis (2000) was adjusted for our biogeochemical interactions. With this code, it is possible to use a streamline oriented grid which makes it possible to prevent numerical dispersion as is intrinsic to rectangular finite element grids. In Figure 1, the comparison of analytical (stochastic advective approach) and numerical solutions is shown for the case of zero transversal dispersion.

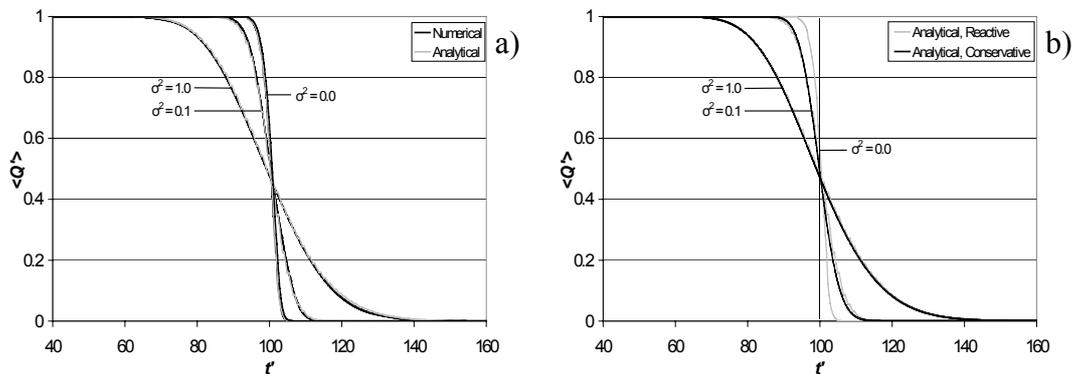


Figure 1: Comparison between analytical and numerical solutions (a) and between analytical results for nonreactive and reactive transport (b). Shown are breakthrough curves at a control plane of initially resident retarded contaminant that is degraded according to Monod kinetics in the presence of injected electron acceptor. Shown are results for three variances of the random hydraulic conductivity (From Janssen et al., submitted, 2004).

It appears that the agreement between the analytical and numerical solutions is excellent, where the analytical solution takes the local TW shape (of Keijzer et al., 2000) in each stream tube into account. The comparison between reactive and nonreactive breakthrough curves reveals that in case of some heterogeneity of the flow domain, the local TW solution may be ignored and replaced by a plug displacement approximation, as heterogeneity dominates.

An equally good agreement between numerical and analytical results was obtained if pore scale dispersion was taken into account (not shown), using the approximation of Cirpka (2002).

In view of the disagreement between the model results if a rectangular grid is used, it remains disputable whether the stochastic advective approach is or is not applicable. It appears that we may

distinguish two regimes for nonlinear transport in heterogeneous media. For small conductivity variability (or, conversely, for relatively significant transversal dispersion), the exchange between stream tubes appears to be important. In those cases, the flow domain behaves essentially homogeneous, and the macroscopic solute fronts (of contaminant as well as injected chemical) behave as a traveling wave (fixed shape and velocity) after a short transition period. However, for significant variability of the hydraulic conductivity or for small local mixing, heterogeneity dominates, and the local TW is not found for the macroscopic front: the transversally averaged macroscopic front reveals a continuously growing second central moment (i.e., continued spreading).

In Figure 2, the difference between the cases that take or do not take transversal dispersion into account is shown to grow with displaced distance and to be significant in magnitude. This observation has several implications: neglecting transversal dispersion for such cases of nonlinear transport is not justified, Fickian displacement does not develop, and it does not seem that the second central moment for the Advective Dispersive case stabilises (i.e., no TW behavior). Hence, it remains unclear how the macroscopic transport equation should be formulated.

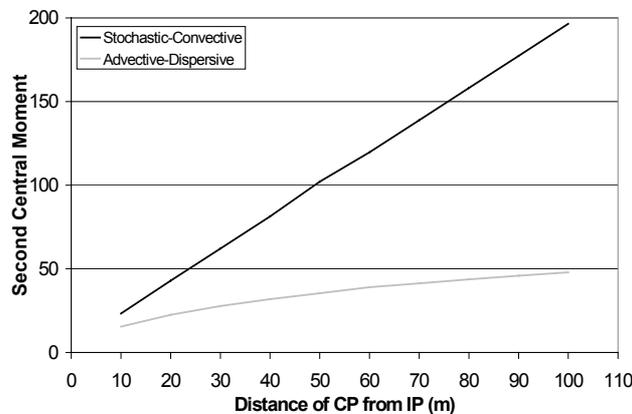


Figure 2: Development of the second central moment of the macroscopic (flow domain averaged) breakthrough curve as a function of travelled distance for the case of zero transversal dispersion (Stochastic Convective) and for finite transversal dispersion (Advective Dispersive). (From Janssen et al., submitted, 2004)

3. Pore Network Modeling

Recently, a similar treatise was given for transport in a pore network where nonlinear Freundlich sorption was assumed, with the intention of assessing how such nonlinearity affects macroscopic transport (Van der Zee et al., 2004). The model (Acharya et al., 2004), called HYPON, resulted also in continuously increasing second central moments for the pore network averaged breakthrough, except for a hydraulically homogeneous network (Figure 3).

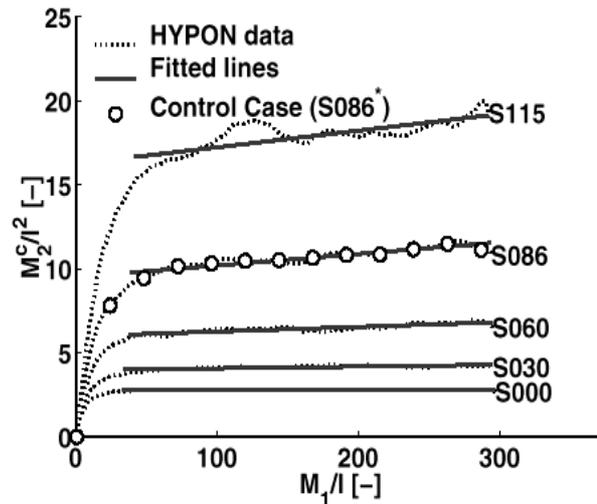


Figure 3: Scaled second central spatial moment as a function of the scaled mean front position, for a homogeneous (S000) and four heterogeneous networks (S115 largest variation coefficient of the pore body size). For case S086, also results are shown for another realisation (S086*). All shown cases have the same mean pore body size. (From Acharya et al., submitted, 2004)

4. Conclusions

For nonlinear interactions in hydraulically heterogeneous media, the second central moment shows two regimes of behaviour. For relatively large transversal mixing, the flow domain acts as if it is homogeneous and TW type of behaviour may develop. For relatively small transversal mixing, heterogeneity dominates, but the second central moment depends on both mixing and nonlinearity. In the second case, a Stochastic Advective approximation may not be justified, a Fickian regime of displacement is not yet ascertained, and the macroscopic transport may not be described with a CDE that is adjusted with a nonlinear interaction term. These analyses (Janssen et al., 2004, Acharya et al., 2004) suggest that it may be necessary to conduct an explicit upscaling, before macroscopic modelling is feasible. Most existing codes for nonlinear transport in ground water may be based on erroneous assumptions with regard to how this upscaling should be conducted.

5. Acknowledgments

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Urban soil pollution and heterogeneity - a question of scale

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Abstract: The objective of the project has been to provide a factual foundation describing the characteristics of diffuse soil pollution in urban areas. Investigation strategies to optimise data collection and predict soil contamination levels in relation to urban age, type of housing, soil fill etc. have been derived. Geostatistical tools and analysis of pollutant patterns have been used to improve the accuracy of these predictions. A close relationship between urban age and elevated levels of lead, zinc, cadmium and PAH/BaP dioxins has been established. Some of the many aspects investigated by field trials have been the mapping of levels of pollution and the measurement of heterogeneity related to the type of pollutant and the source of the diffuse pollution.

1. Introduction

The Agency of Environmental Protection in Copenhagen under the Danish Environmental Protection Agency's Technology Program has instigated a project concerning diffuse soil pollution in urban areas. The objective of the project is to provide background information concerning the characteristics of diffuse soil pollution in urban areas and on this basis to devise appropriate investigation strategies.

2. Material and methods

A preliminary study was carried out to measure data variation for two sampling units of 10 x 10 m (100 m²) in Copenhagen. In table 1, statistical parameters for lead are presented. The two areas show quite clearly different levels of contamination, although a relatively large variation around the median values is seen for unit 1.

Table 1: Measures of central tendency and dispersion for lead in test areas of 100 m².

	Minimum	Median	Maximum	Mean	CV	No. of data
	mg/kg dw				%	
Unit 1	134	221	374	239	27	42
Unit 2	31	43	57	43	15	9

In the main study, over 900 soil samples have been sampled and analysed from 14 historical delineated areas in size ranging from 60,000 – 300,000 m² and representing different sources of pollution in Copenhagen and a provincial town, Ringsted, in Denmark.

Three types of diffuse soil pollution have been investigated in 2002/2003.

- Diffuse soil pollution caused by urban sprawl and related to the type of housing and materials, construction age, emissions from domestic heating, deposition from distant sources, soil fill etc.
- Diffuse soil pollution caused by emissions from traffic
- Diffuse soil pollution caused by atmospheric deposition from nearby industrial sources

The 14 areas are as follows:

- 5 residential areas in Copenhagen (three areas with terraced housing est. in 1600, 1890 and 1930, as well as two modern housing estates from the 1950's and 1960's).
- A reference area (park) lying between two of the oldest residential areas in Copenhagen.
- 5 residential areas in a provincial town - Ringsted (one area with terraced housing from 1880, and four areas with detached housing (villa) from 1915-1920, 1940's, 1950's and 1980's).
- A residential area in an industrial suburb of Copenhagen (housing estate from the 1930's) close to an industrial metal processing facility.
- A 1.6 km section of main road in Copenhagen (est. 1920, 4 lanes, 90 km /h, 50,000 cars / day).
- A 0.7 km section of road in Copenhagen (est. in 1900, 2 lanes, 60 km /h, 20,000 cars / day).

Each residential area is expected to have a characteristic level of diffuse soil pollution, while soil pollution alongside the main roads is expected to decrease with distance from the roads.

The 14 test areas have been investigated using sampling strategies designed for geostatistical data treatment. The objective is to find a method to describe the probable level of diffuse soil pollution for a historical delineated area. All soil samples are analysed for arsenic, copper, chromium, lead, nickel and zinc by X-ray fluorescence (and some control samples by ICP) and by GC-MS-SIM for sum of 7 PAH including benzo(a)pyren (BAP). A subset of samples have been analysed for cadmium, mercury, total hydrocarbons (oil, tar), dioxins, PCB's, phthalates, pesticides and additional PAH (about 30 PAH's including alkyl derivatives) with a view to evaluation of PAH profiles according to source. Samples have been taken from between 1-5 sampling points in sub sampling units of 4 - 100 m², randomly distributed across the area under investigation. This sampling design allows a geostatistical data treatment, since it provides many data points at small distances to each other. Samples have been taken from 0-5, 2-10, 20-30, 45-55 and 95-105 cm's depth, but mostly in 2-10 cm's depth. Point sources of pollution have been avoided. No composite samples have been prepared and each soil sample has been analysed individually with a number of replicates in each area. Geostatistical and statistical tools have been applied in the data treatment.

3. Results and discussion

The background for the investigations and the detailed account of the investigations and conclusions concerning strategies and typical levels of urban pollution are described in Falkenberg & Riis, 2002, Falkenberg et al. 2002a, 2002b, 2004a, 2004b, 2004c, 2004d and Falkenberg et al. 2003.

The most critical pollutants are lead and BaP since the soil quality criteria (guidance level) for sensitive residential land use (40 and 0.1 mg/kg dw respectively) are exceeded in most of the test areas. For these two pollutants, intervention criteria for soil pollution have been defined at 400 and 1 mg/kg dw respectively.

The data from many of the test areas does not appear to be normally distributed and a log normal transformation is required. For some substances, the data is skewed to the right (many low values often due to low levels around the detection limits) and for other substances skewed to the left (many elevated values). For nearly all areas, a few very high values are present. To describe the data, the mean, median, minimum, maximum and selected quantiles are calculated. Quantile plots, which makes no assumptions about the data distribution and show all data points giving a graphical representation of the data, are used for a visual presentation of the data, US EPA, 2000. The geostatistical data treatment requires comparison of variance for pairs of data at different distances. To estimate the nugget effect, which describes the combined sampling and analytical variation for samples taken from the same position, it is necessary to have sufficient data points at small distances to each other. The sampling variation in each sub sampling unit and across the delineated area describes the micro/macro scale heterogeneity of pollution in the soil and the spatial distribution.

One aspect of the study was to evaluate if the use of composite samples could improve the investigation strategy and/or reduce the cost of investigation. In Fig. 1, the individual content of lead and BaP in individual samples taken from a sub sampling unit of 100 m² is compared to the value for a theoretical composite. Some sub sampling units have a uniform level of pollution, while other units demonstrate a wide range of values. In Fig. 2, the difference between the median (value to the left of box-whisker plot) and mean (value to the right of box-whisker plot) calculated on the basis of 12 composite samples is compared with the values based on 12 randomly selected individual samples. Essentially, the use of individual samples would not affect decision-making if median values are used for decision-making, whereas the mean values show a greater dependence on the choice of individual samples. Calculations based on more than 12 samples would give a better estimate.

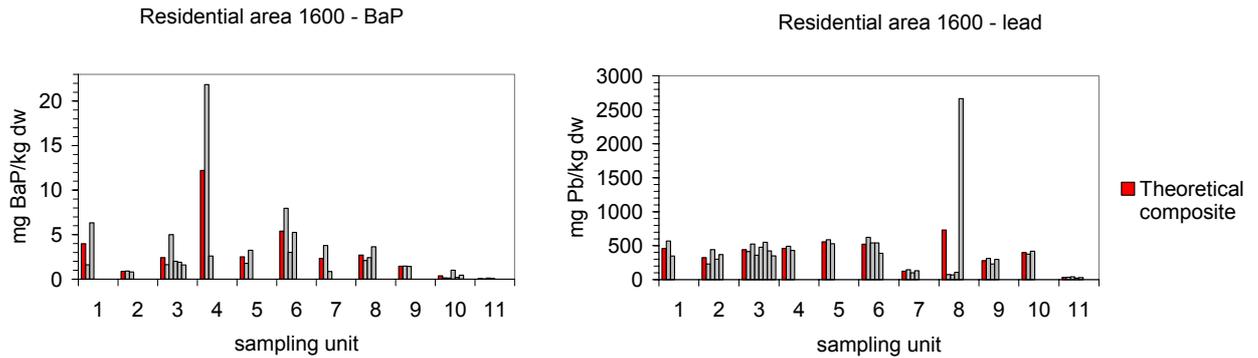


Figure 1: Comparison of individual samples and a theoretical composite for sub sampling unit.

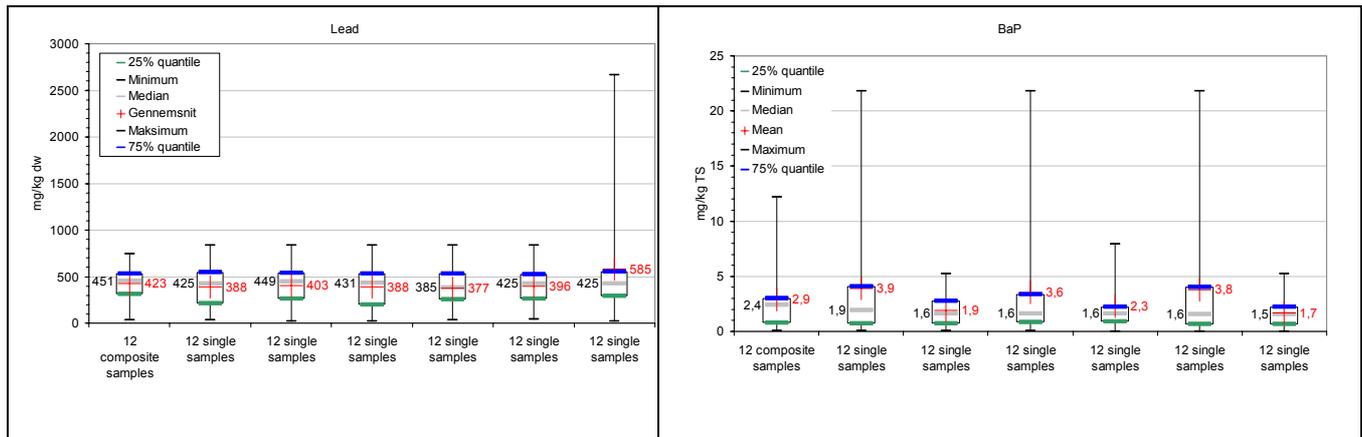


Figure 2: Effect of choice of samples on median and mean values.

Information concerning variation is of importance to the geostatistical evaluation and the use of composites is less interesting if a geostatistical approach, i.e. the measurement of variance, is to be attempted, since the cost of preparation of a composite is today comparable to the cost of analysis and fewer samples can be analysed. Composites can of course be prepared representing small sub sampling units, i.e. 1 m² at small distances to each other, but this increases the cost of the investigation with little benefit, whereas increase in the number of analysed samples is of great benefit.

For the 12 residential test areas, the range of values is of course much greater than seen in the individual sub sampling units. Generally, very old areas have experienced redevelopment (demolition, soil excavation and construction of newer housing) and they exhibit large variation in data values as illustrated in table 2. The area illustrated in table 2 had to be divided in zones before a lognormal dataset could be identified. In these kinds of areas, intensive sampling at the level of individual properties is required, if a precise level of characterisation is required. The applied investigation strategy allows identification of areas with a high degree of heterogeneity allowing additional

investigations to be instigated if required, although these are usually unnecessary with regard to decisions concerning the general level of diffuse soil pollution.

Table 2: Measures of central tendency and dispersion for lead and BaP in an old residential area.

Residential Est. 1600	Minimum	Median	Maximum	Mean	CV %	No. of data
	mg/kg dw					
Lead	23	350	2665	384	105	49
BaP	0.003	0.25	3.3	0.431	137	39

However in areas with little redevelopment, the diffuse soil pollution has shown a more uniform pollution load and a characteristic pollution pattern could be identified and distinguished from other areas with a different history, construction type, location or age for housing development. This is illustrated in table 3 and 4 for two residential areas both established in 1880, but differing in location.

Table 3: Comparison of measures of central tendency and dispersion for lead in two test areas

Residential-terraced	Minimum	Median	Maximum	Mean	CV %	No. of data
	mg/kg dw					
Copenhagen 1880	55	210	770	284	64	39
Provincial town 1880	20	56	150	60	56	15

Table 4: Comparison of measures of central tendency and dispersion for BaP in two test areas

Residential-terraced	Minimum	Median	Maximum	Mean	CV %	No. of data
	mg/kg dw					
Copenhagen 1880	0.023	1.5	2.7	2.13	90	23
Provincial town 1880	0.42	1.0	5.6	1.97	79	15

In Fig. 3, the quantile plots for lead and BaP are also compared for these two areas. A clear difference in lead levels is seen, whereas the levels of BaP are comparable. Equally clear is the fact that most lead data values lie below the intervention level, whereas the intervention level for BaP is exceeded in a majority of samples from both areas. Hotspots with BaP are indicated in both areas by a few samples with extreme elevated values.

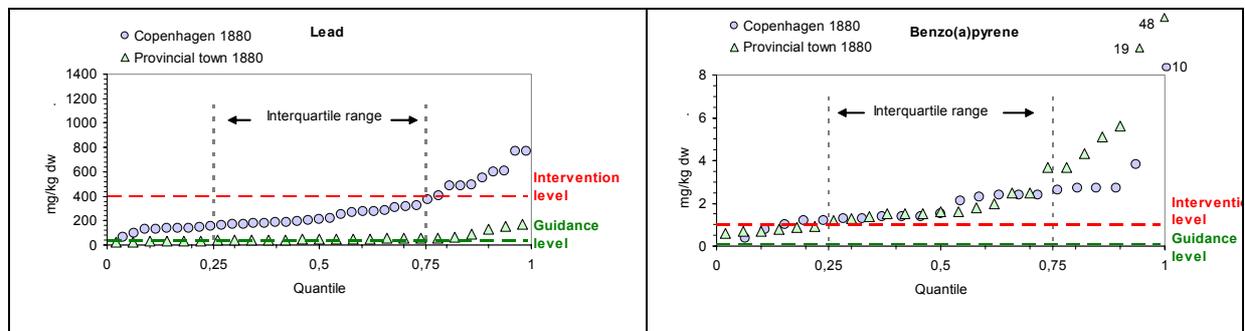


Figure 3: Comparison of two test areas by quantile plots.

4. Conclusions

In the course of this project, a close relationship between urban age and elevated levels of lead, zinc, copper, cadmium and PAH/BaP has been established as visualised in Fig. 4.

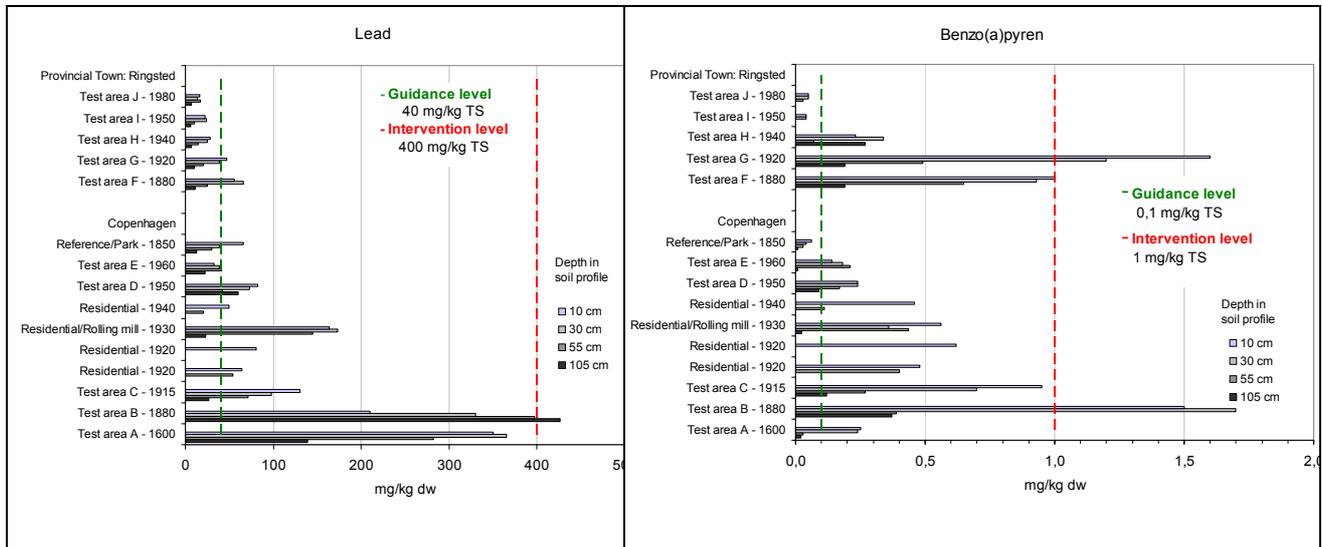


Figure 4: Comparison of median values for lead and BaP in areas of differing urban age and location

Some areas do however exhibit a large range of concentrations. The study also confirmed that pollutant levels for heavy metals and PAH/BaP are not correlated. Impacts from the other parameters are negligible, but background levels have been established.

It seems unlikely that difference in pollutions loads in the different areas can be attributed to proximity to main roads as hitherto was assumed. The reference area exhibits very low levels compared to the adjacent test areas A and B. Furthermore, the soil pollution due to emissions from traffic and wastewater from the road surface shows highly variable, but elevated levels of lead, copper, zinc and PAH/BaP close to the road verge, but fall to background levels within 20 m of the road as illustrated in Fig. 5.

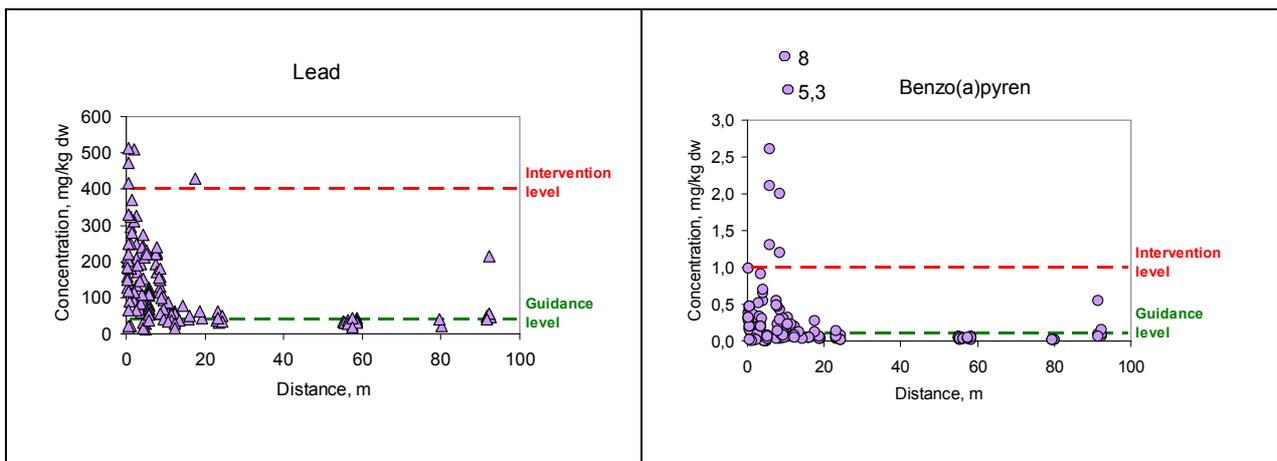


Figure 5: Concentration profiles for lead and BaP in 10 cm depth at a distance from a road.

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Herbicide transport and vulnerability of a shallow groundwater: local and regional scale study

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Abstract: The herbicide transport processes and the groundwater (GW) vulnerability to chemical contamination were studied in a portion of the alluvial aquifer of the Rhône River Valley located near Martigny (Southwest Switzerland). Local transport experiments were associated to a regional monitoring of the groundwater over a two year period. At the local scale, transport through the vadose zone of two herbicides (atrazine and isoproturon) was studied in detail. Water flow and solute transport are closely linked to climatic factors. After the application, the pesticides remain at the soil surface. Following the first heavy rainfall, the chemicals are quickly transported through the vadose zone and may reach the groundwater in a very short time. During subsequent dry periods, concentrations decrease steadily throughout the whole soil profile. After further rainfall events new attenuated concentration peaks are detected in the groundwater while only very small peaks are observed in the unsaturated zone. At the regional scale (400 ha), pesticides were detected in groundwater samples collected in 13 piezometers, sometimes at high concentration, but during a short period of time (mid May to mid July). A few weeks after the application, the chemical concentration in the groundwater corresponds to the background values. Regional observations are in good agreement with the conclusions of the local experiments (rapid transport, important influence of the climatic conditions, quick decrease of concentration peaks); the fate of the herbicides reaching the GW is strongly influenced by the groundwater characteristics.

1. Introduction

Herbicide transport processes and groundwater (GW) vulnerability to chemical contamination were studied in a portion of the alluvial aquifer of upper the Rhône River Valley, between the city of Martigny and the village of Charrat, in the Valais canton (Southwest Switzerland). The aquifer is generally unconfined. The water table lies within 1 and 2 m below the soil surface (Di Gioia, 2002). The groundwater flows more or less parallel to the Rhône River in a westerly direction with an average gradient of 1‰. The soil layers consist mainly of sand and silt near the surface, and of coarser material in the lower part of the profile. The organic matter content as well as the clay content are generally low (< 2 and < 10%, respectively). The saturated hydraulic conductivity varies between 10^{-4} and 10^{-6} m/s, the bulk density between 1.20 and 1.53 g/cm³ and the porosity between 0.42 and 0.66 cm³/cm³. The average annual precipitation is about 700 mm. Evapotranspiration increases from February to July, so that the water balance is negative during summer (Soutter, 1996). Fruit trees, vegetables, and corn cover most of the surface within the plain, while vineyards predominate on the slopes with some isolated orchards. Herbicides are applied to the fields once or twice a year. The time of application differs according to the crops: vines are generally treated in March, fruit trees from late April to early May and, if necessary, again in late July or August, corn is typically treated in late June. Farmers use different commercial herbicide products, such as simazine and diuron for vineyards, simazine, diuron, and terbutylazine for fruit trees, and atrazine for corn. Vegetables are sometimes treated with simazine or terbutylazine, but many other substances are also used. It is extremely difficult to know precisely the quantity of herbicides applied by the farmers.

The purpose of the study was to study in detail the fate of two herbicides from the soil surface to the groundwater table and to gain a better understanding of the risks of contamination of the alluvial aquifer. The investigations were based on local transport experiments associated to a regional monitoring of the groundwater over a two year period.

2. Material and Methods

At the local scale, four plots (plots 1 to 4) were installed (Meiwirth, 2003; Meiwirth and Mermoud, 2002), each of which was 2.50 m long and 1.60 m wide. The plots were instrumented at the beginning of April 2001 (TDR probes and suction cups were installed at 10, 30, 50, 70, and 100 cm depth and tensiometers at 10, 20, 40, 60 and 85 cm depth). Additionally, stainless steel piezometers were installed on two of the plots and a rain gauge was placed near the plots. Two herbicides (atrazine and isoproturon) were applied two consecutive years at relatively high concentration (3 to 4 times the recommended dose) and the transport through the vadose zone was studied in detail.

At the regional scale, the observation area (400 ha) was equipped with 13 piezometers and groundwater samples were collected regularly in order to determine the concentrations in 5 selected herbicides (atrazine, terbuthylazine, simazine, isoproturon and diuron). The piezometers were installed along four transects (Fig. 1): two longitudinal transects (T1 and T2) and two transects transversal to the groundwater flow (T3 and T4). The piezometers, screened from the first upper meter, consisted of 3 to 4 m long stainless steel tubes with an outer diameter of 64 mm. Groundwater samples were collected approximately every 2 weeks from May to August and once a month in winter time. In 2002 weekly samples were taken in June and July.

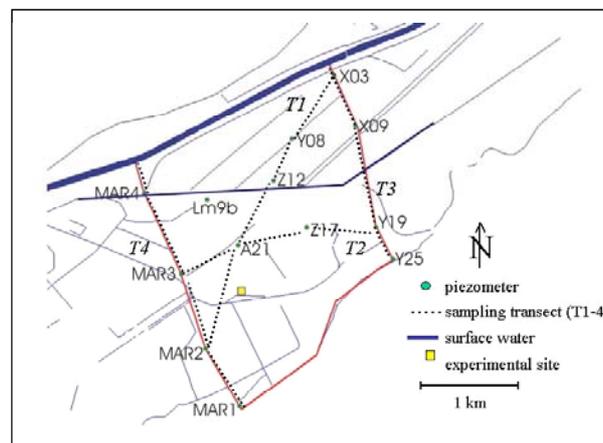


Figure 1: Observation area, location of the piezometers and of the transects

3. Results

3.1 Local scale experiments

Soil moisture and hydraulic head profiles attest that during dry periods, water moves from the groundwater to the soil surface through capillary rise, while during and shortly after rainfall, water flows to the groundwater table. Whatever the climatic situation, the water content remains extremely high over the entire profile and is constantly greater than $0.28 \text{ cm}^3/\text{cm}^3$, even near the soil surface.

The transport of atrazine and isoproturon through the unsaturated zone was monitored during the months following application in May 2001 and 2002. Based on the experience gained in 2001, a more efficient sampling scheme was implemented in 2002; accordingly, the interpretation will focus mainly on observations made in 2002.

Fig. 2 shows the temporal concentration changes of isoproturon measured in the suction cups at different depths on plot 4 (results were similar on the other plots). During the two dry weeks following the application, the concentrations in the unsaturated zone remained low. After the first important rainfall event (June 5), high concentrations appeared at 10, 30, and 70 cm depth. Surprisingly, the concentrations remained low at 50 cm suggesting bypassing of the suction cup. The concentrations decreased steadily during the following dry period and a second small concentration peak was

observed at 10 cm after further rainfall at the end of June. From July on, the concentration remained low over the whole profile. Atrazine presented a similar behaviour.

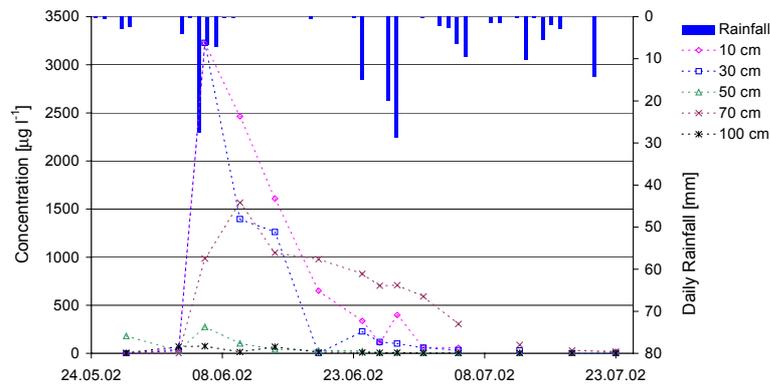


Figure 2: Isoproturon concentration in the suction cups at different depths (plot 4, 2002) and daily rainfall (secondary axis)

Fig. 3 presents the herbicide concentration in the groundwater and the evolution of the GW depth. The temporal changes of the chemical concentration are remarkably similar to the fluctuations of the groundwater table. No chemicals were found in the GW during the first two weeks after the application characterized by an absence of significant rainfall. A sudden peak appeared in the GW as a consequence of the precipitation on June 5. The concentrations decreased during the following weeks and a second concentration peak appeared after the heavy rainfall of the end of June. A third attenuated peak was observed in mid July. The concentration evolution of the two herbicides was very similar.

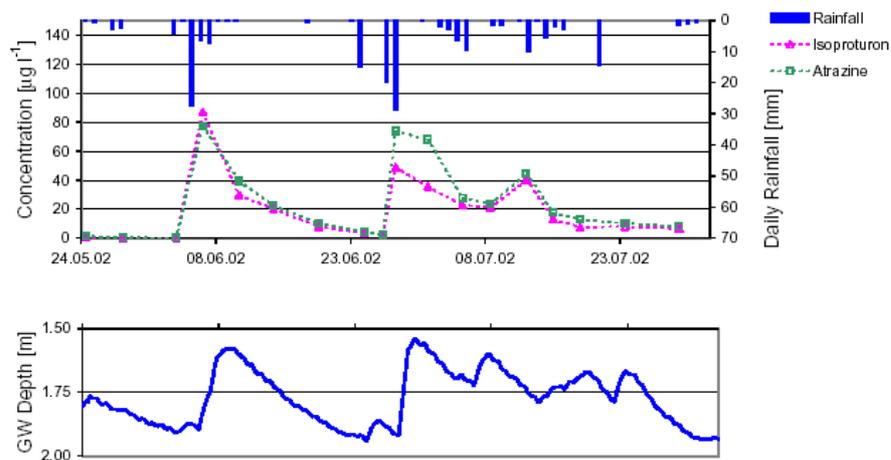


Figure 3: Herbicide concentration in the groundwater (plot 4, 2002) and depth of the groundwater table

3.2 Regional observations

During the two years of the study, GW samples were collected in the different piezometers and the concentration in 5 herbicides (atrazine, simazine, terbutylazine, isoproturon, and diuron) was determined.

Herbicides were detected in the groundwater in all the piezometers. Maximum concentrations were

observed during a short, critical period in 2001; throughout the rest of the year, the concentrations remained below the drinking water limit of $0.1 \mu\text{g l}^{-1}$. In 2002, considerably lower concentrations were detected.

Fig. 4 shows, as an example, the atrazine concentration in different piezometers. High concentrations were measured in late June 2001 after the first important rainfall events subsequent to the herbicide application. During that period, high concentrations of atrazine were measured in several piezometers situated within the plain and near the slope (MAR2, MAR1, Y25, Y19). On the other end, only very slight increases in concentration were detected in the piezometers located near the Rhône river (X03, X09, MAR4).

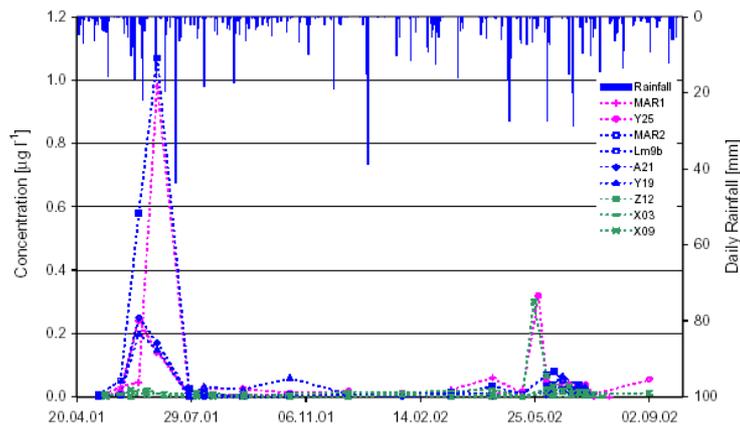


Figure 4: Evolution of atrazine concentration in different piezometers of the observation area

The highest concentration was measured in MAR2, a piezometer located on a corn field to which atrazine had been applied in 2001. In 2002, the field was not subject to herbicide application and the concentrations remained low; that same year, atrazine was detected at concentrations lower than $0.1 \mu\text{g l}^{-1}$, except in piezometers Y25 and Z12.

The most frequently encountered substances were atrazine, simazine and terbutylazine; isoptoturon and diuron were detected locally during peak periods at relatively low concentrations. The spatial distribution of the herbicide concentration was found to be closely linked to the GW characteristics. Near the Rhône river, high hydraulic head gradients quickly dilute chemicals brought from the above fields and herbicides coming from more distant fields may also be detected. Near the slope, inflow of contaminated water from the hillside (vineyards) can contribute significantly to concentration peaks. Within the plain, relatively high concentrations in the herbicides applied to the above located field can be observed temporarily. Fig. 5 presents, as an example, the concentration in different herbicides measured along transect T3 during the peak period of late June 2001.

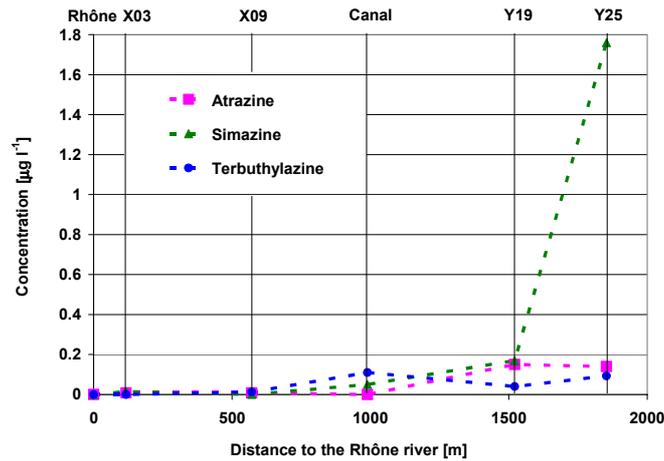


Figure 5: Herbicide concentration along the transect T3 in late June 2001

4. Conclusions

Intensive measurements during two years on the experimental plots demonstrated that the water flow and the chemical transport are closely linked to the climatic conditions. As long as no water is applied to the soil, the chemicals remain near the soil surface. After the first rainfall event following the application, herbicides are quickly transported through the vadose zone into the groundwater. During dry periods, the concentrations decrease steadily in the soil profile and the groundwater. After further rainfall, additional concentration peaks are observed in the groundwater, while only small peaks appear in the unsaturated zone.

At the regional scale, herbicides were detected in all the piezometers, sometimes and for some of them at high concentrations, but during a short period of time (mid May to mid July). A few weeks after the application, the chemical concentration in the groundwater is near the background values, below the drinking water limit. The observations are in good agreement with the conclusions of the local experiments (rapid transport, important influence of the climatic conditions, quick decrease of concentration peaks). Furthermore, the groundwater characteristics play an important role on the fate of the herbicides reaching the GW. Near the Rhône river, high hydraulic gradients quickly dilute chemicals leaching from the above fields and herbicides coming from more distant fields may also be observed. Near the slope, an inflow of contaminated water from the hillside (vineyards) can contribute significantly to the groundwater contamination. Within the plain, high concentrations of herbicides applied to the above located fields can be observed temporarily. Contaminations are confined in time and space and different substances are detected from one piezometer to another.

5. Conclusions

This research was undertaken within the scope of the European project PEGASE (Pesticides in European Groundwaters: detailed study of representative aquifers and simulation of possible evolution scenarios; EU contract number: EVK1-CT1999-00028). The funding of the research by the Swiss Government under the 5th Framework Programme is gratefully acknowledged.

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**SESSION IV:
SCREENING AND MONITORING TOOLS
AT DIFFERENT SCALES**

KEY NOTE:

Estimating the scales of variation for monitoring soil

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Introduction

The general problems of designing efficient sampling schemes for estimating values of soil properties, not only pollutants, in regions large and small have taxed soil scientists for many years. Regional means and their associated variances can be estimated from random samples; the underlying theory was established in the 1930s. But investigators and agencies responsible for monitoring change and implementing statutes want to know more; in particular they want to know *where* there are excessive concentrations of pollutants and potential toxic chemicals. This implies local estimation and perhaps mapping of the variation, which in turn means knowing on what spatial scale or scales the properties of interest vary so as to sample at a suitable density. Sampling the soil to detect and estimate local change within regions is likely to be expensive, and so it is important to know in advance what those scales are so that sampling can be designed rationally to represent the variation.

The variogram

The variogram of geostatistics, and specifically its distance parameter(s), can quantify the spatial scale(s) of variation. Soil scientists have put it to use increasingly in the last two decades, mainly as a step towards local estimation by kriging, but also for description and understanding and for designing sampling regimes. They have treated soil properties as the outcomes of stationary random processes. If a process is second-order stationary then its variance is bounded, and its variogram has at least one distance parameter defining the range or effective range of the process. Places within the range have values that are correlated; the values of those further apart are not—they are independent. So to estimate local values one should have 10 to 16 sampling points lying within the effective range from each target point, and sampling should be dense enough for that.

The isotropic spherical variogram is typical of a second-order process. Its formula is

$$\begin{aligned} \gamma(h) &= c \left\{ \frac{3h}{2a} - \frac{1}{2} \left(\frac{h}{a} \right)^3 \right\} \text{ for } h \leq a \\ &= c \text{ for } h > a, \end{aligned} \tag{1}$$

in which $\gamma(h)$ is the semivariance at lag distance h , and c is the variance of the process. The distance parameter a is the range, defining the spatial scale of the process. So, for estimation at some point, say \mathbf{x}_0 , we should want 10 to 16 points closer to \mathbf{x}_0 than a and ideally a few of them should be closer than $a/2$.

A more elaborate model might combine two such functions:

$$\begin{aligned}\gamma(h) &= c_1 \left\{ \frac{3h}{2a_1} - \frac{1}{2} \left(\frac{h}{a_1} \right)^3 \right\} + c_2 \left\{ \frac{3h}{2a_2} - \frac{1}{2} \left(\frac{h}{a_2} \right)^3 \right\} \quad \text{for } h \leq a_1 \\ &= c_1 + c_2 \left\{ \frac{3h}{2a_2} - \frac{1}{2} \left(\frac{h}{a_2} \right)^3 \right\} \quad \text{for } a_1 < h \leq a_2 \\ &= c_1 + c_2 \quad \text{for } h > a_2 .\end{aligned}\tag{2}$$

This is the double spherical function in which there are now two ranges, a_1 and a_2 . Finding values for these parameters depends on one's having sample values of $\gamma(h)$, i.e. a sample variogram, for several values of h less than a in Equation (1) or less than a_1 in Equation (2). The model is then fitted to the sample variogram.

Estimating the sample variogram can still require substantial sampling, and unless you know approximately the value of a (or a_1) you might under-sample with sampling intervals that are too large and so have no estimates of $\gamma(h)$ less than a , as did Oliver and Webster (1987), or sample excessively with short intervals and incur unnecessary expense. Evidently, it would be an advantage to know roughly at what scale the property varies before one embarks on such an exercise. As it happens we can do this by adapting classical analysis of variance of a nested sample.

Nested sampling and analysis of variance

The hierarchical analysis of variance was originally developed to determine the variance attributable to each of several levels of classification of a population. Youden and Mehlich (1937) saw its potential in soil survey for estimating the contributions of the spacings between sampling points to the total variance and so design more efficient surveys. For a sampling scheme with m stages the components of variance sum to the total variance in the data:

$$\sigma^2 = \sigma_1^2 + \sigma_2^2 + \sigma_3^2 + \cdots + \sigma_m^2 .\tag{3}$$

Webster and Butler (1976) took the technique a stage further by accumulating the components of variance of soil properties to form variograms, thus:

$$\begin{aligned}\sigma_m^2 &= \gamma(d_1) , \\ \sigma_{m-1}^2 + \sigma_m^2 &= \gamma(d_2) , \\ \sigma_{m-2}^2 + \sigma_{m-1}^2 + \sigma_m^2 &= \gamma(d_3) ,\end{aligned}\tag{4}$$

and so on, where d_1 is the shortest distance at the m th stage, d_2 is the second shortest distance at stage $m - 1$ and d_m is the longest distance at the first stage.

Webster and Butler sampled a region of Australia the soil of which had proved difficult to classify and map. Their design had spacings at 5, 18, 56 and 180 m. Table 1 lists the accumulated components of variance (the variograms) for several properties of the topsoil. From it we see that by far the largest proportion of the variance in potassium comes from spacings between 56 and 180 m. We could sample at, say, 50-m intervals to map the pattern. For phosphorus, in contrast, almost 80% of the

variance occurs within 5 m, and clearly we could not afford to sample sufficiently densely to resolve the intricacies of the pattern. We could, however, treat the region as homogeneous and compute simple means, and so we have obtained valuable guidance from this modest reconnaissance.

Table 1. Proportions (as percentages of total) of variance deriving from spacings 5, 18, 56 and 180 m at Ginninderra in the Australian Capital Territory (from Webster and Butler, 1976)

Spacing/m	Soil property			
	Bulk density	pH	Available P	Exchangeable K
5	48.8	22.6	79.1	3.3
18	63.2	42.7	87.4	7.6
56	68.0	66.5	87.4	12.3
180	100	100	100	100

Oliver and Webster (1987) resorted to this technique after failing initially to identify the scale of variation in their survey. They also adapted the design so as to embody more than the four stages to which Youden and Mehlich (1937) and Webster and Butler (1976) had limited themselves without an exponential increase in the effort (Oliver and Webster, 1986). The resulting design was unbalanced, but this is a small penalty to pay for the gain in resolution.

Wavelet analysis

The underlying variograms of geostatistics are of intrinsically stationary random functions, and the analysis of variance, though robust, is based an assumption of homogeneous variances. These assumptions might seem weak, but even they can be untenable where the land surface crosses parent materials of different origin and geomorphic history and where local topographic variation causes marked differences in drainage status. They are also likely to be violated near sources of pollution. In these situations not only do the means of soil properties fluctuate, but so do the variances, which seem to change both in magnitude and spatial scale and to have locally transient features. Standard geostatistical technique cannot cope, and the outcome of an analysis of variance might be misleading.

To describe variation of this kind mathematicians have developed a new set of techniques based on wavelets. Wavelets are families of compact analysing kernels that are passed over sequences of data and are convoluted with them.

A wavelet has the general formula:

$$\psi_{\lambda,x}(u) = \frac{1}{\sqrt{\lambda}} \psi\left(\frac{u-x}{\lambda}\right), \quad \lambda > 0, \quad x \in \mathcal{R}, \quad (5)$$

where \mathcal{R} is the set of real numbers. Thus the wavelet within any one family has two characteristics, its width or scale, λ , which is set to 1 for the mother wavelet, and its

position x , which is set arbitrarily to 0 for the mother wavelet. Increasing λ dilates the wavelet; decreasing it shrinks the wavelet.

The mean in all cases is zero, i.e.

$$\int_{-\infty}^{\infty} \psi(x) dx = 0, \quad (6)$$

and the squared norm is 1:

$$\int_{-\infty}^{\infty} |\psi(x)|^2 dx = 1. \quad (7)$$

The wavelet also has a compact support, by which I mean that the mother wavelet damps rapidly to zero away from its centre.

The wavelet is passed over the data and integrated with them in steps for each position x . This gives the wavelet transform, $Wf(\lambda, x)$:

$$\begin{aligned} Wf(\lambda, x) &= \int_{-\infty}^{\infty} f(u) \psi_{\lambda, x}(u) du \\ &= \int_{-\infty}^{\infty} f(u) \frac{1}{\sqrt{\lambda}} \psi\left(\frac{u-x}{\lambda}\right) du. \end{aligned} \quad (8)$$

The scale parameter is changed and the convolution is repeated. Further, for each combination of λ and x we can compute a variance.

Among the families of wavelets those of Daubechies (1992) are especially attractive because if the scale is varied in multiples of powers of 2, i.e. $\lambda_m = \lambda \times 2^m$, then the resulting m transforms are orthogonal. The transforms can therefore be separated and used to filter data, and they can be recombined for any combinations of the λ s. Also, we can see both at what scale and where variance is contributed. This should enable us to distinguish ‘hot spots’.

The applications in soil and environmental science are still tentative, partly because of the novelty and partly because many data are needed, especially in two dimensions. The latter difficulty might be overcome by remote sensing. Once we know where most of the variation is then we can concentrate subsequent sampling there. Lark et al. (2004) have recently shown how this might work after analysing measurements of N₂O escaping from soil and discovering both where most of this green-house gas is being generated and where the emission is most variable.

Conclusions

Designing efficient sampling schemes for monitoring soil or other features of the environment more generally requires prior knowledge of the scale(s) of variation. This knowledge itself can be obtained only by sampling. A staged approach is recommended, as follows.

1. Start with a nested scheme and hierarchical analysis of variance to identify the principal spatial range within which the variance occurs.
2. Follow this by sampling at regular intervals within that range and compute and model the variogram(s).

3. If the variance appears to fluctuate widely so that the assumptions underlying the variogram are untenable then consider wavelet analysis for identifying both the scale(s) of variation and the localities.

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Possibility of using magnetometry in a European Soil Monitoring System

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Abstract: In the frame of a future discussion of a EU-Soil-Strategy, one of the most important and urgent needs is to establish the Europe-wide monitoring network for soil quality assessment. The spatial variability of soils as well as the variability of soil contamination is very high. Therefore, a relatively dense measurement network is needed. Also the multi-functionality of soil requires more integrated approaches involving issues such as spatial planning, critical loads, and ecosystem analysis. The tools of spatial analysis as well as geo-referenced data such as high-resolution soil maps and digital evaluation models should be used. It is difficult to obtain these goals with traditional, chemical monitoring techniques. One of the major tasks for future monitoring is the development of efficient and cost-effective soil monitoring tools. Magnetometry is the fast, simple, and cost-effective geophysical methods used for the measurements of topsoil magnetic susceptibility that is mostly the result of urban and industrial dust deposition. Anthropogenic dusts are sources of many pollutants in topsoils. Because of low costs of on-site measurement and high spatial resolution of magnetic signals, a relative dense monitoring network can be applied. This can lead to a considerable reduction of the number of samples and chemical analysis limited only for areas of detected anomalies where the high concentrations of soil pollutants create the potential ecological threat. Mapping of spatial distribution of anthropogenic dust deposition and fast identification of soil magneto-geochemical anomalies can be helpful for the location of representative monitoring points within the monitoring network and can serve as an early warning system.

1. Introduction

The cost effective monitoring methods based on in situ measurement are strongly recommended by the Water Framework Directive (2000/60EC) for monitoring programs. Also in reports prepared during the ongoing work on the development of a soil monitoring directive as a major building brick of the soil thematic strategy, the cost efficiency of monitoring methods are several times mentioned. This monitoring directive, when implemented, should deliver data that should allow reviewing and adjusting the EU soil policy at regular intervals, in order to increase its effectiveness. The Monitoring Mandate gives the obligation for Working Groups to evaluate the efficiency of measures already in place.

To support the development of efficient and cost-effective soil monitoring tools in the European Soil Monitoring Network, soil magnetometry based on topsoil magnetic susceptibility measurement was proposed. Until present, magnetic susceptibility has only been used in relative measurements in order to outline areas with different pollution levels or to discriminate between polluted and clean areas but no quantification was attempted. Magnetic screening of large areas, as the >100.000 km² of the MAGPROX project with a grid-size of 10 x 10 km (Magiera et al. 2003) cannot provide such a quantitative approach because of variable contributions by many different pollution sources with different relative magnetic signals. However, on regional and local scales with little variation in the constitution of pollutants and their accompanying magnetic signals, semi-quantitative estimates are possible. Case studies with higher grid-densities (1 km by 1 km and smaller) in Upper Silesia (Poland – Strzyszc and Magiera 1998, 2003) the so-called black triangle area (East Germany – Appel et al. 2003) and in Leoben area (Austria- Hanesh and Scholger, 2002), show strong positive correlations of magnetic susceptibility of top soils and soil profile columns with heavy metal concentrations. Moreover, the method has already been adopted on regional scales for soil (pollution) characterisation in collaboration with national or regional soil surveys. The next logical step is, to adopt and incorporate the method into standard monitoring system on EU level for environmental screening and monitoring.

2. Description of methodology

The conceptual background for the magnetometry is the fact that all soils possess magnetic properties, which are mainly controlled iron and a group of iron-bearing minerals. Magnetic susceptibility (κ) is a very sensitive for the classification of materials and for identifying even trace amounts of highly magnetic minerals such a magnetite. In addition to the natural content of iron-bearing minerals, the accumulation of magnetite-rich anthropogenic magnetic particles in soils gives a significant contribution to topsoil κ values. Magnetic minerals themselves are not hazardous to human health or to ecosystem functioning. However where natural sources are unlikely, the anomalous presence of magnetic minerals may indicate anthropogenic impacts such as deposition of atmospheric dusts and aerosols generated by industrial processes. The magnetic iron oxides emitted from iron works and power plants are a poorly ordered material mainly containing high concentration of heavy metals which will possible be released in the near future because of the thermodynamically instability of the compounds (Hiller 2000).

Magnetometry as a cost-effective and fast proxy method was tested on different scale, on different geological background, and in areas with different anthropogenic dustfall. For data acquisition a Bartington MS2B susceptibility meter was used in combination with a GPS system for geographic positioning. Standardised procedure for site selection, recording of site-relevant information, and for the measurement process were developed and tested to guarantee repeatable and comparable results of individual measurements (Schibler et al. 2002).

During this study, on the base of statistic analysis a considerably high positive correlation between κ values and concentration of some heavy metals (Pb, Zn, Cd, Cu) was found. The correlation was especially high in areas of relatively high industrial and urban dust deposition that was identified as geochemical and magnetic hot spots (Magiera et al. 2003).

To discriminate effects of anthropogenic pollution from natural background values, topsoil cores of 30 cm depth were taken using a Humax soil corer. Enhanced susceptibility values close to soil surface (Of, Oh horizons) indicate anthropogenic (atmospheric dust deposition) input, whereas κ values increasing with depth indicate natural (lithogenic) origin. For this purpose, an instrument for “in situ” measurement with high resolution of κ signal was developed and adopted for magnetometry within the Usefulness of magnetometry for European Soil Monitoring System.

3.1. Representative site selection

In case of soil monitoring crucial aspect is to choose parameters, which will be representative for monitoring site. The list of parameters which have to be considered is usually long and the most important are: land using, type of soil, characteristic landscape units, and different pollution exposure. In case of heavy metal contamination monitoring the amount of annual dry and wet deposition is very important.

The classical monitoring is based on representative sites however the actual European soil monitoring strategy is based on the concept of regular grid-system based on existing 16 x 16 km grid for forest soil monitoring (with planned further developing on agricultural areas) or based on 18 x 18 km grid of LUCAS (Land Use – Cover Area From Statistical Survey) Program covering all existing land use types. This is rater soil survey than classical monitoring system (tab. 1). Even in the frame of regular-grid system the represenatitvity of the site has to be taken into consideration.

Table 1: *Main differences between soil monitoring and soil survey*

Issue	Soil monitoring	Soil survey
Site selection	Based on a representative distribution due to for example: characteristic landscape units, different pollution exposure, land use and soil types.	Based on a regular grid-system
Number of sites	Few	Many
Investigation	Intensive investigations, comprising comprehensive environmental measurements	Commonly a very limited number of measured parameters.
Interval of measurements	Mainly yearly measurements, in some cases shorter intervals.	Not required in general, usually time-interval of several years.

High resolution magnetic screening based on “in situ” measurement in area of planned monitoring site enable to characterise a spatial variability of κ value, which is result of anthropogenic dust deposition. This pre-screening may help to find the most homogeneous site and to define its representativity by using the geostatistic methods. On the base of magnetometric measurements it is also possible to verify the proper localisation of already existing monitoring sites to avoid the local “hot spots” (sometimes several meters in diameter). During the data processing for cartographical presentation such “hot spots” considerably influence spatial distribution of measured parameter on the final map, generating “virtual” anomalies of much larger spatial range than they exist in reality.

3.2. Increasing of cost-efficiency by reducing the number of chemical analysis (level I)

In case of applying of regular 16 x 16 km grid-system for European Soil Monitoring System, in basic monitoring level there will be 19 890 monitoring sites on area of 25 countries of the extended EU. According to EUROSTAT calculation the estimated cost of basic study of minimum parameters essential for Level I was ca. 10,000 €. Among them the laboratory cost of chemical analysis such elements as As, Cd, Cr, Cu, Hg, Mo, Mn, Ni, Pb, Zn were calculated for ca. 4,000 €. Such extremely high costs could be reduced by reducing the number of parameters essential for reliable site assessment or by partial replacing them by less expensive proxy “in situ” methods.

It seems to be not necessary to use chemical analysis of all mentioned above heavy metals in all measurement sites of regular grid-system. In some areas, where the observed contamination level (estimated on the base of existing archival data) was since many years much below the European standards and where is a lack of reasonable circumstances for sudden increase of their content, the chemical analysis can be replaced by systematic control measurement of κ value, that is a reflection of anthropogenic dust deposition including many heavy metals. The chemical analysis would be started again when unambiguous increase of this parameter within the measuring period will be observed.

3.3. Frequency of magnetometric measurement

As soils are relatively static and magnetic particles are very stable, so the repetition of measurement is not necessary earlier than 10 year period. On the other hand, there is evidence that diffuse contamination from atmospheric deposition of metals is difficult to detect over intervals less than 10 years. Only in areas where the increase of anthropogenic influx is expected due to establishing the new pollution source (new factory, motorway etc.) or in areas being after sudden pollution events (e.g.: floods) the repetition may be more frequent (for instance 5 years). In the last case the magnetometry can serve also as a kind of early warning system for control the spreading of pollution.

3.4. Monitoring of local soil contamination (hot spots) – level II

It is obvious, that in areas of local contamination hot spots the basic monitoring network will require more intensive examination with obligatory chemical analysis for individual pollutant content. Also the sampling network has to be denser than basic grid. But also here, to optimise the sampling procedure it has to be preceded by magnetic pre-screening. The analyses of topsoil magnetic

susceptibility distribution in hot spot area can more precisely point at the potential local maxima of contamination where the potential threats are the highest. Consequently, sampling planning (including sampling locations, sampling depths, and the grid density of sampling) can be properly selected and thus remarkably reducing the expensive and laborious methods.

The other aspect is to monitor the soils in areas with expected environmental changes, like new constructed factories, motorways, airports etc. Here, the dense network for magnetometric measurement can be established and the measurement can be done frequently (even annually) to record any changes of susceptibility. The noticeable susceptibility enhancement would be a signal to start the sampling procedure for detailed geochemical laboratory analysis to control the individual pollutants concentration.

3.5. Magnetometry in DPSIR scheme

All the mentioned above situations describe the actual state of pollution and are placed in the third cell of the DPSIR (Driver-Pressure-State-Impact-Response) scheme. However, magnetometry can be also adopted to control the pressure and response.

The pressure could be controlled by record of anthropogenic (industrial and urban) dust deposition using the system of containers full of clean diamagnetic sand or clay with initial susceptibility close to zero that is exposed for dust deposition. Measuring in regular time periods the increase of susceptibility, the level of dustfall can be controlled. In case of considerable increase of dust deposition in monitoring sites, a decision for starting more detailed investigations of the individual pollutants such as heavy metals can be made.

Also the land filling processes and some remediation processes resulting in decrease of the content of anthropogenic magnetic particles can be controlled by magnetometric measurements.

4. Conclusions

1. Magnetometry can be a useful measurement technique to locate the representative monitoring sites in soil monitoring system or within the regular grid of soil survey.
2. Magnetometry allows to detect and to delineate local and regional patterns of pollution to minimise the number of soil samples essential for assess the actual state of soil contamination. This heads towards the increasing the costs efficiency by remarkably reducing the expensive and laborious chemical analysis.
3. The repeated application of the screening scheme, or certain elements of this scheme allows to monitor in regular time intervals, after remediation measures, or after pollution events (e.g. floods).
4. In areas with relatively low contamination level the repetition of measurement could be not earlier than 10 year period. Only in case of hot spot areas or sudden pollution events the repetition has to be more frequent.
5. Not only the actual state of pollution but also some elements of pressure and response could be estimate by magnetometry.

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Artificial Neural Networks: tools for the optimisation of chemical and biochemical sensors

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1. Introduction

In modern analytical chemistry data evaluation plays an important role. Artificial neural networks are an interesting and powerful tool for the evaluation of data of chemical and biochemical sensors. In this work the principles of neural networks are presented and an example of the efficiency of fully connected and optimised neural networks is given.

2. Methods for data evaluation and sensing devices

2.1 Principles of Artificial Neural Networks

Artificial neural networks are parallel information processing systems. They consist of a number of simple neurons which are organised in layers and connected by links. The networks imitate the brain with its highly interconnected structures. In Figure 1 a scheme of a multilayer feedforward neural network is shown [1].

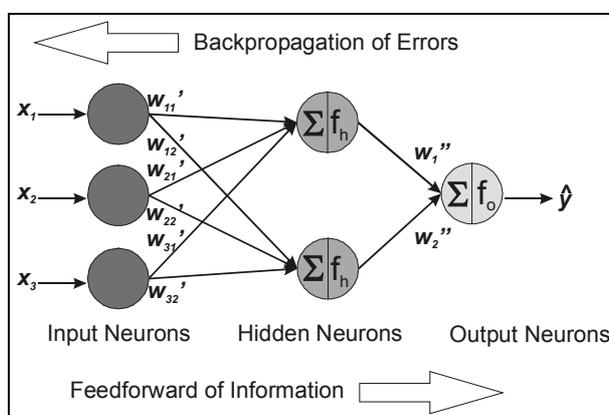


Figure 1: Scheme of a feedforward backpropagation network

The input variables (sensor signals) are presented to the neural network at the input neurons. The input variables are distributed by the connection links to the hidden layer. The hidden neurons sum the weighted signal and project this sum on an activation function f_h , e.g. hyperbolic tangens. The resulting activations are sent via links to the output neuron. A linear function is used as activation function of the output neuron. The weights are the adjustable parameters, which are determined by a learning algorithm during the training procedure of the neural networks. During the training, calibration samples with known concentrations (response variable y) are passed through the network and the deviance between predicted and real concentration is calculated. The resulting errors of prediction are used to adjust the parameters of the net in a backpropagation step to minimise the error. These two steps are repeated until an acceptable low error is reached. The training algorithm tries to

find a minimum on the error surface, whereby in most cases only a local minimum of the error surface is found.

2.2 Topology and Training of Artificial Neural Networks

Neural networks can model several responses simultaneously. Therefore, it is possible to use separate networks with one single output neuron for each analyte to be quantified or to use a neural network with as many output neurons as analytes.

For the training of neural networks many different learning algorithm exist, which can be considered as an optimisation problem. One of the most modern gradient algorithms is the Rprop (resilient propagation) algorithm. These kinds of algorithms follow the steepest descent of the error surface in the hyperspace of the adjustable parameters. The weights are adapted on the sequence of the signs of the derivatives. Due to its speed this algorithm has been successfully used for several chemometric applications. Further the scaled conjugate gradient algorithm (SCG) has been proved to be very efficient with respect to convergence speed and optimisation quality. This algorithm makes use of the pseudo second derivative. Recently, genetic algorithms have been applied for training of neural networks. They are global optimisation algorithms. Drawbacks of these genetic algorithms are the long computing times and the many possibilities in fine-tuning of the weights and biases. These problems have been overcome by a combination of genetic and gradient algorithms.

To avoid overtraining of neural networks, an early stopping mechanism is applied, therefore the calibration data is monitored by a crossvalidation procedure. An overtrained network learns a small data set by heart and loses its generalisation ability. The training is stopped when the error of crossvalidation starts going up.

2.3 Setups

As example, measurements with two different optical sensing principles have been chosen here.

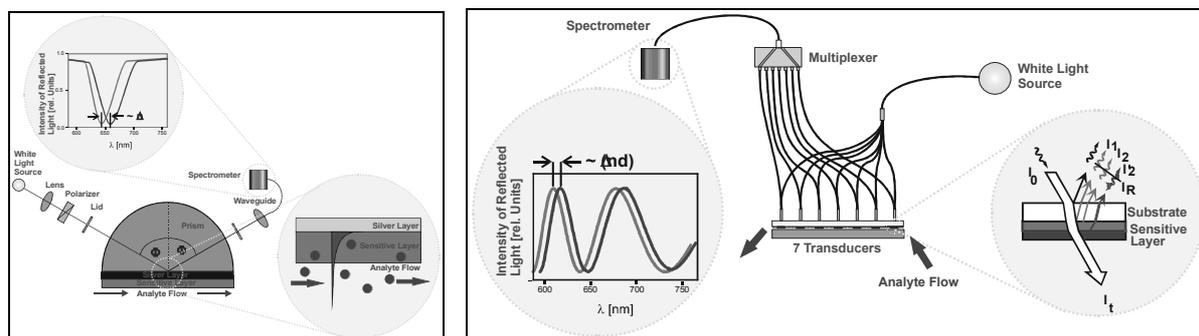


Figure 2: Schematic of the Surface Plasmon Resonance setup (left hand side) and the Reflectometric Interference Spectroscopy setup (right hand side)

The first principle used is surface plasmon resonance (SPR). Surface plasmons are excited at the back surface of a metal layer by parallel-polarised white light. The resonance wavelength of the surface plasmons is mainly influenced by the refractive index of a sensitive polymer layer which is coated on top of the metal layer. Changes in the refractive index can take place due to the interaction of analyte molecules with the polymer layer. These shifts are detected by a diode array spectrometer.

The other principle presented here is the reflectometric interference spectroscopy (RIFS). The interference pattern of white light, which is reflected at phase interfaces, is evaluated. The interference is caused by partial beams which have travelled different paths before reflected at the interfaces. Changes of the optical thickness $n \cdot d$ (product of physical thickness and refractive index) of a sensitive polymer layer can be detected as shifts of the maxima and minima of the interference pattern.

3. Example for the data evaluation with neural networks

An example of time-resolved measurements with SPR and RIFS single sensor setup using the ultra-

microporous polymer Makrolon for the quantification of quaternary mixtures is presented here [2]. The interesting property of Makrolon is interaction behaviour with analytes of different size. Smaller analytes can sorb faster in the polymer layer than bigger analytes. A discrimination of analytes due to different size of the analyte molecules is possible.

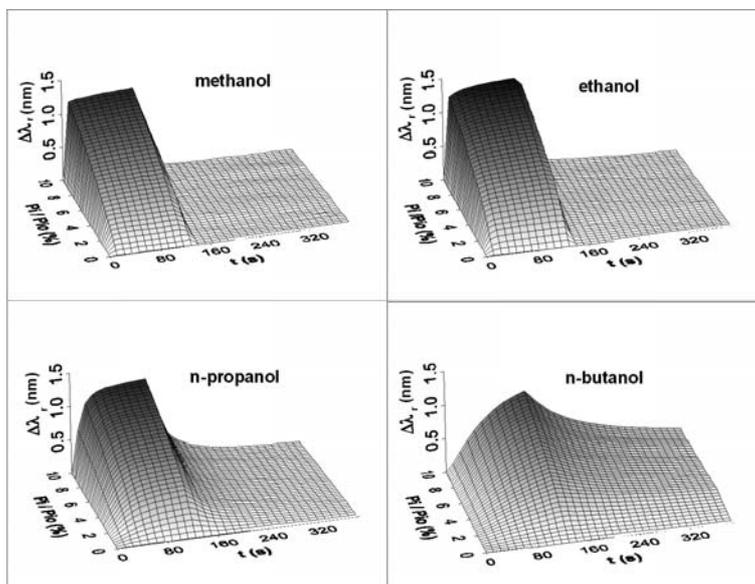


Figure 3: Sensor responses of the pure analytes for SPR-measurements recorded during 150 seconds of the exposure to analyte and exposure to dry air afterwards

For the four homologous alcohols methanol to n-butanol, the sensor responses of the SPR setup is shown in Figure 3 during 150 seconds of analyte exposure and exposure to dry air afterwards. For a quantitative determination of analyte mixtures the interaction kinetic has to differ for the complete concentration range of interest. The smaller molecules of methanol and ethanol immediately sorb into the polymer and desorb very fast resulting in a rectangular shape of the sensor response. The bigger molecules of n-propanol and n-butanol show a slower kinetic resulting in a curvature of the sensor response. The time-resolved approach does not need to wait until equilibrium between the analytes and the polymer layer has been reached. This allows shorter measurement times.

Two multicomponent data sets were recorded for the multicomponent analysis of the quaternary mixtures. The first data set was a 4 level full factorial design. The concentrations of the analytes were varied between 0 and 0.1 p_i/p_{i0} in equidistant steps. This data-set was used for the training of the neural networks and the feature selection process. Further it will be referred as calibration data set. The second data-set was a three-level equidistant full factorial design with relative saturation pressures between 0.015 and 0.075 p_i/p_{i0} . 337 concentrations were measured in total. All measurements were performed in random order.

Many different neural networks based data evaluation strategies have been applied to the quaternary mixture. On the one hand fully connected feedforward neural networks have been applied and on the other hand neural networks with variable selection and genetic algorithm has been successfully applied to the quaternary mixtures [3, 4]. Separate networks were used for all four analytes. Different network topologies were systematically investigated by varying the number of hidden layers and the number of neurons in the hidden layer. The best topology for the analytes has been evaluated by the lowest crossvalidation error of the calibration data set.

In Table 1 a comparison of the relative root mean square errors (RMSE) in % is given for non-optimised and growing neural networks. As can be seen, the errors for all four analytes are low and therefore the predictions of the unknown concentrations of the validation data by the neural networks are good. The optimisation of evaluation by growing neural networks shows even better results for the prediction of the validation data set.

Table 1: Relative RMSE in % for non-optimised and growing neural networks for RfS and SPR

Method	Methanol	Ethanol	Propanol	Butanol	Mean
RfS, growing neural networks	12.5	10.5	12.6	18.1	13.4
SPR, non-optimised networks	9.6	11.0	16.4	19.0	14.0
SPR, growing neural networks	5.8	6.5	10.2	16.0	9.6

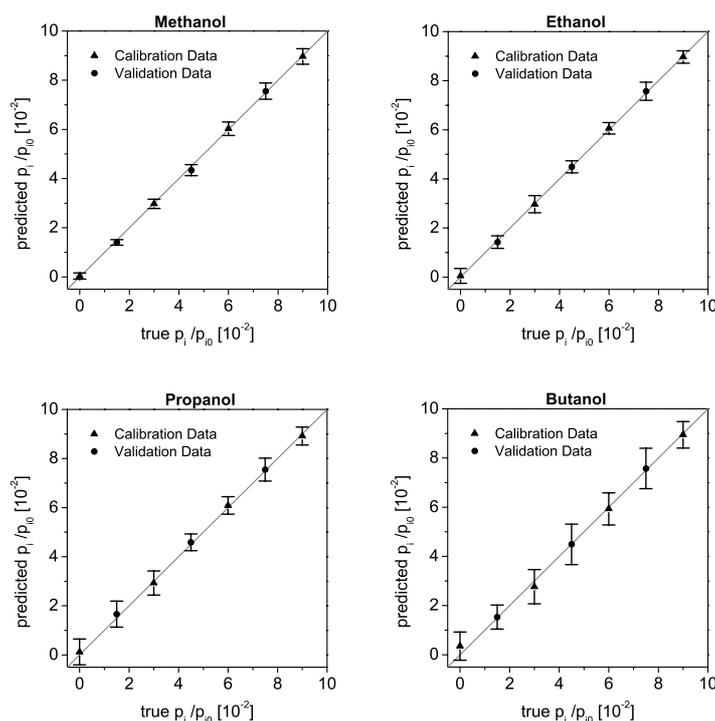


Figure 4: Prediction of the validation data by growing neural networks

In Figure 4 true-predicted plots for the four analytes are shown. In these plots the concentration predicted by the neural networks is plotted versus the true concentration of the component. It can be seen that the prediction of the validation concentrations are good over the whole regarded concentration range. No systematic error is observed and the standard deviations are very low.

4. Conclusions

The ability for quantification of multi-analyte mixtures with artificial neural networks has been demonstrated in the given example. By the use of different strategies for the neural networks an optimisation of the evaluation can be obtained. However, neural networks are a powerful tool for the evaluation of chemical and biochemical sensors.

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**SESSION V:
MANAGEMENT OPTIONS FOR LARGE SCALE SOIL
AND WATER POLLUTION INCLUDING
ENVIRONMENTAL ECONOMICS AND SOCIO-
ECONOMIC ISSUES**

KEY NOTE: Global-scale scenarios and modelling as tools for managing large scale nitrogen pollution

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Abstract: UNEP's GEO Yearbook 2003 characterizes problems related to reactive nitrogen (nitrogen overloads in some areas and nitrogen deficiencies in other areas of the globe) as an emerging global environmental issue. Global modelling and scenario analysis may help to investigate linkages and feedbacks between global change and water pollution, and to identify appropriate management options.

To get an overview of the present-day global situation of nitrogen input and fate and to derive scenarios of the future that simulate the impact of global change (climate, population, agriculture, waste water treatment, etc.), the global model WaterGAP-N is being developed. WaterGAP-N will simulate the input and fate of terrestrial nitrogen, including the input from diffuse (industrial fertilizer and manure, biological fixation, and atmospheric deposition) and point sources, and the transport of dissolved N and its loss by denitrification in soil and groundwater as well as in surface waters (rivers, lakes, wetlands). With a spatial resolution of 0.5°, the model computes the N loads in each cell as well as the input to the oceans. Here we present first results of WaterGAP-N and show how the model will be used to derive management options for large-scale nitrogen pollution on the background of the SRES scenarios of the Intergovernmental Panel on Climate Change (IPCC).

1. Introduction

Scenarios can help to understand the consequences of today's decisions in a quite distant and uncertain future. They describe a range of consistent and plausible images of alternative futures in an integrated manner, considering the most important driving forces of the socio-environmental system of interest. State-of-the-art environmental scenarios combine qualitative with quantitative elements, i.e. storylines with model calculations. The development of qualitative-quantitative scenarios may consist of the following steps (Döll, 2004):

- Identification of the problem field and the participants of the scenario process
- System definition including driving forces as well as temporal and spatial resolution and extent
- Definition of indicators of the system state
- Development of qualitative reference scenarios in the form of storylines
- Development of quantitative reference scenarios using mathematical models
- Assessment of the impact of management decisions against the background of the reference scenarios
- Evaluation of the scenarios.

Environmental scenarios are always interdisciplinary and have to consider linkages within the social-environmental system. Spatial linkages (transport processes) or temporal linkages (buffer and transformation processes) generally produce an even higher degree of complexity.

Nitrogen pollution has been recognized as a large-scale problem that does no longer affect only developed countries (UNEP, 2002). Due to the future increase of population and wealth, and the related extension and intensification of agriculture, even larger areas of the globe will potentially be subject to high nitrate levels in the groundwater and the eutrophication of surface waters (terrestrial and marine). Global modelling and scenario analysis may help to investigate linkages and feedbacks between global change and water pollution and to identify appropriate management options. In

particularly global modelling helps to explore linkages between food consumption in one region and environmental effects in another one.

In order to assess management options for large-scale soil and water pollution, it would be ideal to derive integrated quantitative scenarios of various pollutants (nitrogen, phosphorus, pesticides, salt etc.). These scenarios would be based on mathematical models, which relate driving forces (population, food consumption patterns, climate etc.) and specific management options with the level of pollution. For efficiency and consistency reasons they should rely on existing global change scenarios (SRES report by the Intergovernmental Panel on Climate Change (IPCC), Nakicenovic, 2000). The SRES scenarios describe the future world development in four scenario groups along a matrix of the attributes *global* versus *regional* and *economic* versus *environmental* and provide consistent scenario assumptions with regard to major driving forces like demographic change, social and economic development and rate and direction of technological change, which are also relevant driving forces of water and soil pollution. However, it is necessary to complement the SRES scenarios by assumptions specific to pollutions of soil and water.

As a first step towards integrated global scenarios of water and soil pollution we are developing WaterGAP-N, a global model of terrestrial N-input and fate. This model is specifically designed for use in scenario development.

2. Development and first results of the WaterGAP-N model

WaterGAP-N simulates the amount of nitrogen transported by rivers into the world's oceans by first computing diffuse and point sources of reactive nitrogen and then its transport through soil, groundwater and surface waters (rivers, lakes and wetlands) to the ocean, taking into account denitrification losses. The model uses monthly time steps and covers the whole land area of the globe (except Antarctica), with a spatial resolution of 0.5° longitude by 0.5° latitude (approximately 67,000 cells). WaterGAP-N processes information on global land cover, crop distribution and crop productivity as well as information on livestock numbers and productivity as provided by the IMAGE 2.2 implementation of the SRES scenarios (IMAGE Team, 2001), hydrological information as provided by the WaterGAP model (Alcamo et al., 2003) and information from several other sources (Fig. 1).

Since N pollution of ground and surface waters is closely linked to land use and management, it is necessary to consider scenarios of land use to derive estimates of future N pollution. IMAGE 2.2 is the only existing global model that simulates land use as well as productivity of crops and livestock up to the year 2100 consistent with the SRES scenarios. Therefore land use and productivity in WaterGAP-N is based on modified simulation results of the IMAGE 2.2 model although for present day conditions other land use maps, which are based on remote sensing and actual sub-national statistics, would be more appropriate (e.g. Leff et al., 2004).

The part of WaterGAP-N that computes diffuse inputs of reactive nitrogen into ground water is already functioning while the other parts of the model exist as concepts and have still to be developed. First results of the soil nitrogen balance as simulated by WaterGAP-N show that the largest turnover of reactive nitrogen occurs in regions with high plant productivity (Fig. 2a and 2b). In areas covered by natural vegetation or forests most of the N-inputs go into plant uptake, and the highest values of N leaching from the soil are found in intensively used agricultural areas (eastern part of the United States, Western Europe, India and the eastern part of China). Nitrogen leaching has increased between the early sixties and the early nineties in particular in Asia (Fig. 2c and 2d).

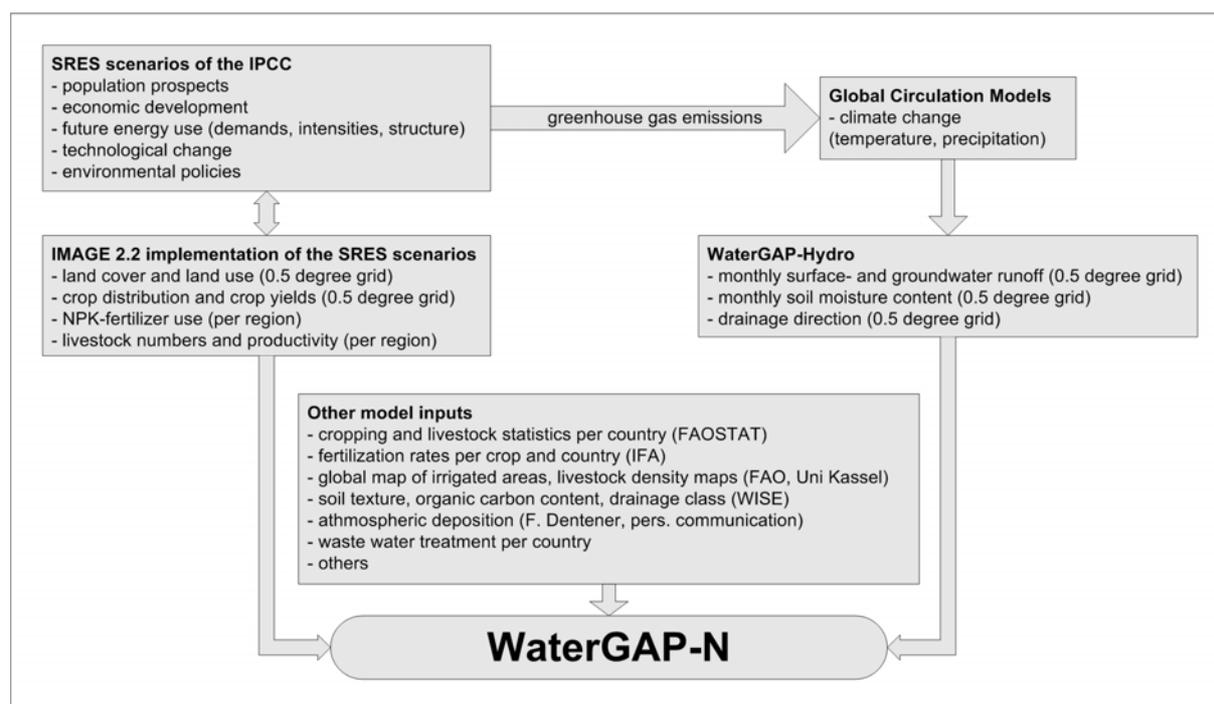


Figure 1: Input data for the WaterGAP-N model.

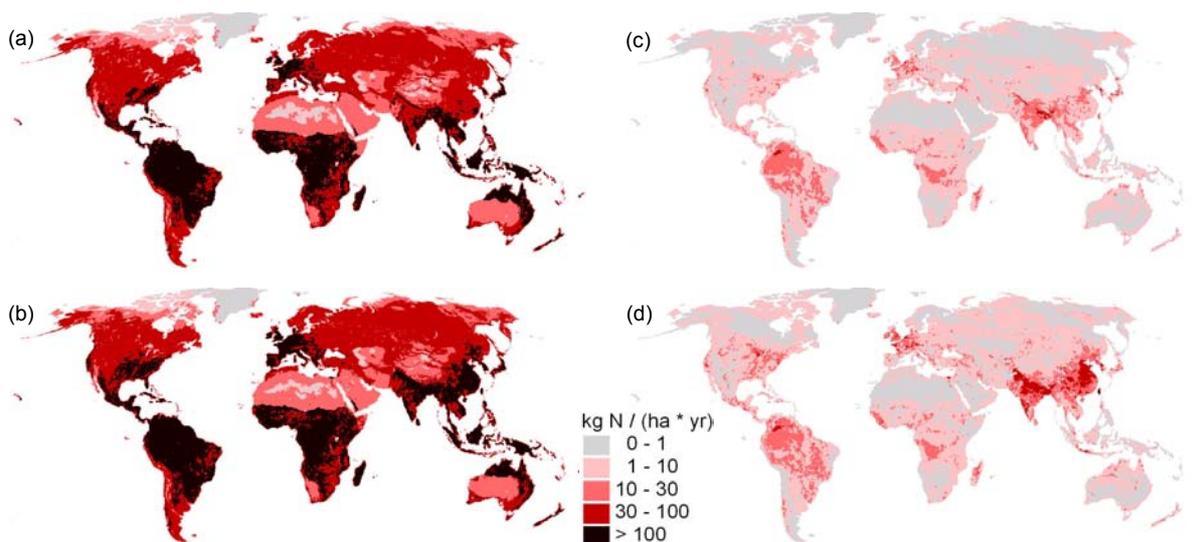


Figure 2: Total diffuse inorganic nitrogen load of the soil (sum of mineralization of organic matter, synthetic fertilizers, deposition, symbiotic N-fixation of crops) and leaching of nitrogen below the root zone as computed by WaterGAP-N ($\text{kg N ha}^{-1} \text{ yr}^{-1}$), a) average annual nitrogen loads 1961-1965, b) average annual nitrogen loads 1991-1995, c) average annual nitrogen leaching 1961-1965, d) average annual nitrogen leaching 1991-1995.

A comparison to results of other global studies indicates that the simulation results of WaterGAP-N are in the range of other existing global models and that even in the global summery the uncertainty of the simulation results is high (Tab. 1). It is very difficult to assess the uncertainty of the results systematically because measurements of N-leaching on such a scale are not possible. Systematic measurements are only available for the nitrogen concentration in the rivers, which is however at the end of the chain of nitrogen transformation and transport processes.

Table 1: Compartments of the nitrogen soil balance as modelled by WaterGAP-N compared to other global studies, values in Tg N yr⁻¹

Source	Sheldrick et al. (2002)	Nevison et al. (1996)	Mosier et al. (1998)	Van Drecht et al. (2003)	WaterGAP-N model		
Base year(s)	1996	1990	1989	1995	average 1991-1995		
Extent	arable cropland	global land area	agricult. area	agricult. area	global land area	agricult. area	global land area
Synthetic fertilizer use	78.2	78.0	79.0	76.5	76.5	73.0	73.0
Manure use*	33.3	102.0	124.2	105.3	105.3	107.7	107.7
Biological N-Fixation	7.7	n.a.	9.7	40.8	159.7	34.8	160.7
Deposition	21.6	n.a.	n.a.	40.8	65.5	n.c.	58.3
Mineralization	n.c.	828.0	n.a.	n.c.	n.c.	n.c.	1147.0
Soil mining	18.3	n.c.	n.c.	n.c.	n.c.	n.c.	17.4
Plant uptake**	101.2	835.0	n.a.	<i>91.0</i>	n.a.	108.9	1101.1
Leaching	n.a.	172.0	n.a.	55.0	n.a.	n.c.	80.2
Denitrification	n.a.	128.0	n.a.	79.0	n.a.	n.c.	158.0
NH ₃ -volatilization	n.a.	n.a.	n.a.	30.0	n.a.	40.3	40.3

n.c. : not considered

n.a. : not available

* : N content before NH₃-volatilization

** : values in italic refer to N-export by the harvested parts of biomass

Because the SRES scenarios and the IMAGE 2.2 model were developed with focus on greenhouse gas emissions and climate change, specific assumptions related to water pollution are missing in the existing scenarios. In case of nitrogen pollution these are in particular:

- Assumptions on the amount and efficiency of waste water treatment,
- Assumptions related to the management of biofuel crops,
- Extent of and specific management in organic agriculture,
- Fertilizer management in agriculture (e.g. type of fertilizer spreading, storage of manure).

To simulate future nitrogen pollution it is necessary to complement the existing scenarios by those and some other assumptions. The range of meaningful assumptions is determined up to a given degree by the specific scenario but active pollution management can also influence it. Therefore options for large-scale pollution management may be those which make sense in the given scenario and also lead to low soil and water pollution.

3. Conclusions

In order to use the WaterGAP-N model to derive options for managing large-scale nitrogen pollution it is necessary to finish model development (including model validation), and to modify and complement assumptions of the SRES scenarios. Then, it will be possible to assess the impacts of e.g. increased population and wealth on nitrogen pollution and to compute, for example, the effect of improved waste water treatment or fertilizer management. However, many management options appear to be related to changing global food consumption and agricultural production and trade patterns. In order to assess such options it would be necessary to first develop an improved global land use model which would then be coupled to WaterGAP-N to obtain scenarios of land use that does not result in excessive N pollution.

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Abatement of diffuse soil pollution by controlling areal mass fluxes from soil to plants

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1. Introduction

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

Sustainable land use requires active or passive control of large-scale diffuse matter fluxes into, within and out of agro-ecosystems. This calls for effective methods and tools to monitor of these fluxes, to assess the effects caused by low-rate large-scale accumulation of pollutants, and to develop strategies and techniques to prevent and decrease this type of pollution. In addition there is the challenging task to treat already affected soils and waters. Successful large-scale and long-term management of material fluxes in agro-ecosystems and of land affected by diffuse low to medium-level pollution cannot be achieved by the same strategies and methods developed for the detection, classification and treatment of hot spot contamination such as hazardous waste sites. It requires the development of suitable tools to:

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

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

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

For this purpose we developed PROTERRA-S, a tool to assess, analyze and model regional-scale heavy metal fluxes in agro-ecosystems, including a stochastic module to evaluate the influence of parameter variability and uncertainty on the variance of the flux estimates. The model calculates metal fluxes and mass balances by land-use classes within the region (stratified by cropping system and farm type) which are then summed up to give the total metal fluxes through the agricultural soils of a region.

Application of the model to a 95 km² test region in north-western Switzerland showed that metal

fluxes in agricultural soils vary considerably in space and time depending on factors such as types of farms, types of cultivation practices, number of animals per unit area, production of animal manure per unit area of farm. For example net accumulation of cadmium was found to vary between 0.6 and 17.8 g ha⁻¹ a⁻¹ and zinc accumulation between 17.9 and 3360 g ha⁻¹ a⁻¹.

3. Management of heavy metal fluxes in agro-ecosystems

Management and regulation of metal fluxes through agricultural soils is focusing on the input side at present, i.e. to the quantity and quality of applied fertilizers and other agrochemicals. Attempts to influence also output fluxes are restricted to the remediation of local hot spots of contamination by means of phytoextraction. These attempts have not met with much success so far, however, because the rates of metal extraction are too low in general to achieve the remediation goal within an acceptable time. Phytoextraction of metals may, however, be very promising if it could be developed into a tool to actively control the transfer of metals from soils into crop plants and respective products. In this way phytoextraction could be used as part of a trace element and micro-nutrient management strategy which is based on the philosophy of metal recycling. We believe that such an approach is probably the only way to achieve the goal of long-term sustainability with respect to diffuse areal fluxes of metals in agro-ecosystems.

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KEY NOTE: Vulnerability for nitrate loading and acid deposition as represented by geochemical districts in The Netherlands

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Abstract: Geochemical districts are areas which behave similarly with regard to pollution, resulting in comparable groundwater chemistries. Recognition of geochemical districts gives a quick assessment of effects of pollution on the chemical composition of groundwater, and conversely also in effects of remedial measures. Moreover, geochemical districts may serve as a starting point for predicting the future chemical composition of groundwater abstracted from phreatic aquifers by waterworks for the public drinking water supply. In this contribution geochemical districts are distinguished in The Netherlands with respect to nitrate loading and acid deposition, but the same approach may be used for estimating the vulnerability of (abstracted) groundwater for pesticides and other chemical pollutants.

1. Introduction

Even in a small country like The Netherlands the chemical composition of phreatic groundwater varies considerably: from groundwater bodies with high nitrate concentration, low hardness and low pH to bodies with high sulfate concentration, high hardness and high pH. Knowing the rationale behind these variations results in the division in geochemical districts (van Beek et al., 2003). Conversely, identification of these districts makes prediction of chemical compositions possible, and consequently also of the chemistry of the abstracted groundwater.

In this contribution districts are identified with respect to nitrate loading and acid deposition. This brings us to the various inputs of nitrate and of acid and to the reactive compounds present in the soil matrix. In this respect the soil may be considered as a reaction vessel with a very variable content and a variable input which results in a wide variety of chemical compositions of shallow groundwater.

2. Sources of nitrate and acid

Nitrogen is added to the soil in many forms: nitrate (NO_3^-), ammonium (NH_4^+), organic nitrogen (R-NH₂), ammonia (NH₃) and nitrogen oxides (N₂O, NO) originating from many sources: (mineral) fertilizer, liquid manure and atmospheric deposition. All of these species will be converted by atmospheric oxygen to nitrate upon deposition.

One in situ source of nitrate results from mineralization of organic matter. In all these sources the counter ion of nitrate consists of a proton; in other words leaching of nitrate is accompanied by leaching of mineral acid.

Another acid generating process takes place in agriculture. Biomass (harvest) contains an excess of cations over anions, the remainder consisting of organic anions. As the uptake of a cation by roots is accompanied by the release of a proton, and the uptake of an anion by the release of a hydroxyl-group, harvest results into a net acid production in the root zone of the soil. In order to prevent development of too low pH values, farmers must neutralize the (mineral) acid produced. This acid is neutralized either by lime present naturally in the soil or added by the farmer. With other words: in agricultural areas leaching of nitrate (and acid) is always accompanied by the leaching of hardness (sum of concentrations of calcium and magnesium).

In natural reserves, in particular in forests, there may be a great acid load due to acidic atmospheric deposition. If the soil naturally contains lime or exchangeable calcium, the excess acid will be converted into hardness. If the soil contains no lime, the acid will be neutralized by aluminum hydroxides, leading to high concentrations of aluminum.

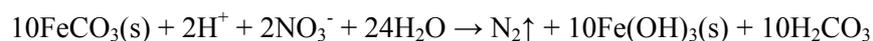
Based upon this description, three land use types are relevant with respect to input:

1. Agricultural areas: leaching of nitrate and acid will always be neutralized by lime, resulting in a high hardness of groundwater.
2. Natural reserves: leaching of acid may be neutralized by naturally occurring lime or exchangeable calcium, otherwise high aluminum concentrations may arise. This holds in particular for wooded areas, and less for grassy areas.
3. Urbanized areas: these areas show no high potential for leaching of nitrate and/or acid.

3. Reactive compounds present in the soil matrix

Sandy soils in The Netherlands consist for 90 to 95% of the inert mineral quartz. Reactive compounds, relevant for the chemical behavior of nitrate in soil and groundwater, present in the soil matrix comprise (labile) organic matter and iron sulfides (pyrite). The behavior of acid soil is governed by the presence of lime and other acid neutralizing minerals and of charged surfaces.

Recently Hartog et al. (2002) demonstrated the presence of siderite (iron carbonate) in sediments. According to Postma (1983) iron carbonates may only develop under very reduced high pH conditions. Denitrification and neutralization of acid by iron carbonates may be represented as:



From this equation it is apparent that this process results into high carbonic acid (carbon dioxide) concentrations. High concentrations of carbon dioxide may also arise from intensive root respiration.

4. Distribution of reactive compounds in the soil matrix

Reactive compounds are not present in all soils, and if present they are not necessarily homogeneously distributed. Distinction should be made between depositional and post-depositional conditions. Sedimentary deposits may contain high amounts of organic matter under "wet" conditions and low amounts under "dry" conditions.

The amount of lime depends on the lime content of the "parent" material: high amounts in river Rhine deposits and no lime in river Meuse deposits. The amount of clay minerals depends on the flow velocity: high amounts in standing waters, and low amounts in fast flowing waters.

After deposition, the sediments will be flushed by groundwater, and leaching of organic matter and lime will start, as will be the formation of iron sulfides (van Beek et al., 2001). Until recently the presence of iron carbonate has only been confirmed to a limited extent, which makes it hard to derive general conclusions.

The rate of leaching depends on the initial content of reactive compounds in the soil matrix, on the chemical composition of the infiltrating precipitation water and, most importantly, on the number of flushed pore volumes. Other conditions being equal, the flow of groundwater will be faster in coarser grained parts of sediments compared with finer parts. This means that the number of flushed pore volumes will be larger in the coarser parts. In the end, the coarse parts of the sediment may be completely leached, while "pockets" of fine material are not. This phenomenon is obvious in intercalated peat-, clay- or loam layers in a coarse soil matrix: these layers contain huge amounts of organic matter, lime and iron sulfides, while the coarse soil matrix is completely leached (Brown et al., 2000).

Based upon the content of reactive compounds in the soil matrix, it is now possible to distinguish three

classes of sediments based upon the degree of leaching:

1. "Old" sediments. These sediments are completely leached. Consequently (shallow) groundwater in this class contains nitrate and aluminum, and thus has a low hardness and low pH.
2. "Young" sediments. These sediments contain organic matter and at some depth iron sulfides. If these deposits contained initially lime, they still do so. This groundwater contains no nitrate, has a high hardness and high pH, and may contain high concentrations of sulfate.
3. "Intermediate" sediments. These sediments are completely leached, except for pockets, which still contain organic matter and lime. In this class a variable part of groundwater has been in contact with reactive compounds. Groundwater in this class contains low concentrations of nitrate and sulfate, and has a variable hardness.

In all these classes (former) waterlogged seepage areas may be present, which contain huge amounts of organic matter and iron sulfides, and occasionally lime.

5. Geohydrochemical districts

Based upon type, content and distribution of reactive compounds present in the soil matrix (van Duijvenbooden and Breeuwsma, 1987), it is now possible to distinguish several geohydrochemical districts in the Netherlands that behave differently with respect to nitrate and acid load. Some characteristics of these districts have been summarized in table 1.

Table 1: Summary of the characteristics of the geohydrochemical districts. Moreover the chemical composition of the abstracted groundwater is indicated, and the number of well fields belonging to each district.

Geohydrochemical district	Reactive compounds present in the soil matrix				Leaching characteristic ¹⁾	Concentration in abstracted groundwater			Number of well fields
	labile organic matter	iron sulfides	iron carbonate	lime		Nitrate	sulfate	hardness	
<i>infiltration areas</i>									
Inert sandy soils	-	-	-	-	+++	+++	nr	-	35
Boulder sand	+ ²⁾	+	+?	+ ²⁾	++	+	+	+	12
Loess	-	-	-?	+++	+++	+++	nr	+++	11
Pyrite containing sands	++	++	-	-	+	+++	+++	-	10
Dune soils	+	+	-	+++	+				4
<i>seepage areas</i>									
Peat soils	+++	+	-?	-	nr	-	-	-	14
Wetlands	+++	++	++	+++	+	-	+++	+++	17
<i>Miscellaneous</i>									
Inert sandy soils surrounded by wetlands						+++	+++	+++	7
Total number of (hydrologically) vulnerable well fields									110

-: not present, no change in concentration; +: little present, hardly leached, small change in concentration: +++: very much; nr: not relevant

1): leaching characteristic is expressed as number of pore volumes flushed

2): present in "pockets"

Fig. 1 shows as an example the distribution of nitrate over the districts (van Beek et al., 2002). From figure 1 large differences in the concentration of nitrate are obvious: these differences are caused by the variance in nitrate loading and by the occurrence of denitrification: complete denitrification in the districts boulder sand and peat, partial denitrification in wetlands and pyrite sand and no denitrification in inert sands. In loess there are apparently well fields without and with complete denitrification. The "mix" group includes waters derived from wetlands and inert sands, the concentration of nitrate being governed by the contribution of both components.

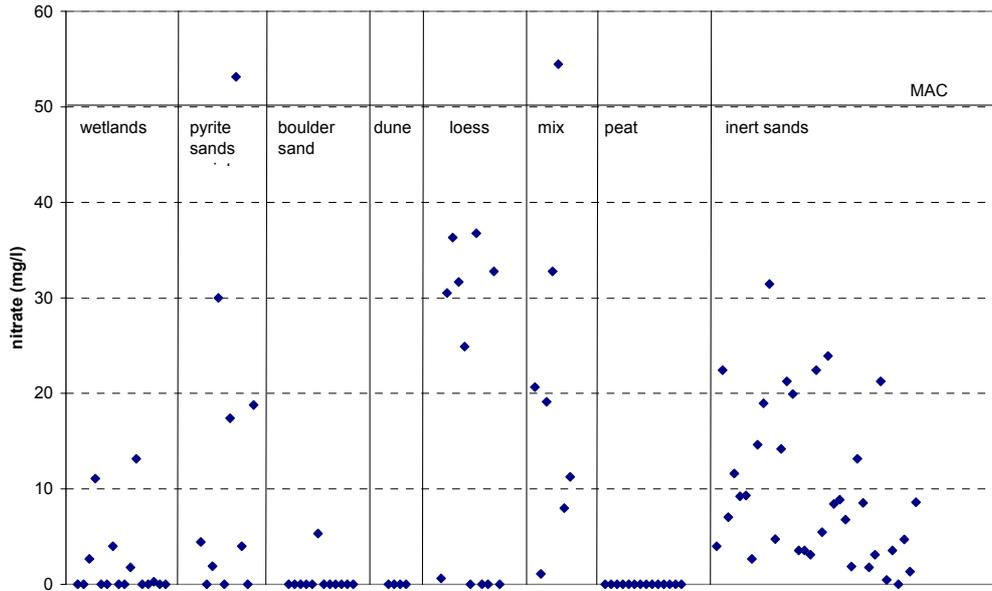


Figure 1: Distribution of the concentration of nitrate in the abstracted groundwater in the various districts. The horizontal axis represents the number of well fields. MAC: Maximum Allowable Concentration for nitrate in drinking water.

Fig. 2 shows the distribution of pH over the districts. High values for the pH are encountered under conditions of complete neutralization of acid by lime and under reducing conditions. This explains the high values for pH in the districts wetlands, loess and peat. Variable values are encountered in the districts boulder sand, inert sands (the high values in this group are pointing towards low carbonic acid concentrations), and in the mix group (the value of pH governed by the proportions of the inert and wetlands group). Low values are encountered in pyrite sands.

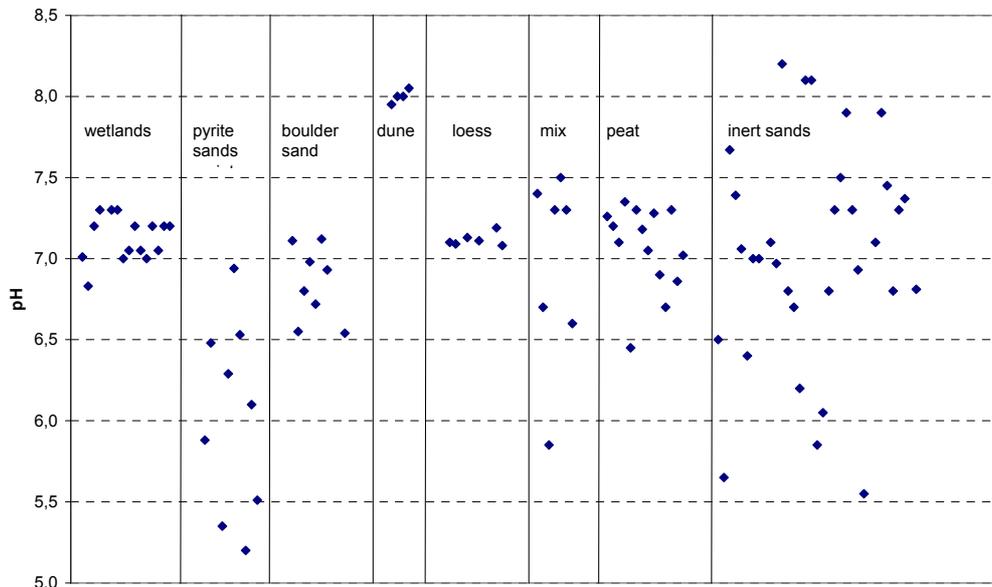


Figure 2: Distribution of the pH in the abstracted groundwater in the districts distinguished. The horizontal axis represents the number of well fields.

6. Conclusions

1. Hydrologically vulnerable well fields are characterized by a relatively short response time. The chemical vulnerability is determined by the interaction of a pollutant and the reactive constituents present in the soil matrix. For this reason a classification of well fields based on these reactive compounds into geohydrochemical districts is worthwhile, as the well fields belonging to the same class will all show a comparable behavior. This approach is also worthwhile for an assessment of relevant measures, as the measures will all act similarly on all well fields belonging to one district. The same holds for seepage water feeding (small) surface waters.
2. As the chemical composition of the water at the input side (water leaving the root zone) is similar, the chemical composition of the abstracted groundwater or of the seepage water, will be determined by the presence of reactive compounds in the traversed soil matrix. In this respect the soil is considered as a chemical reaction vessel with an unknown composition.
3. The presence of labile organic matter, lime, iron sulfides (pyrite) and iron carbonate (siderite) appears of paramount importance. Based upon the content and the (homogeneous or heterogeneous) distribution, it appears appropriate to divide The Netherlands into 8 geohydrochemical districts relevant for nitrate and acid vulnerability.
4. Greater diversity of traversed soil environments increases the number of possible pollutant-soil interactions, and reduces the vulnerability of a well field for pollution.

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Assessing the economic impacts of soil degradation: a literature survey

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Abstract: The authors have conducted a survey of economic studies that have assessed the cost of soil degradation in Europe. The aim of this was twofold: first, to assess the availability of economic data on soil degradation, and secondly, to develop a methodology for a comprehensive assessment of soil degradation trends and their economic impacts. The study has been conducted with a view to ongoing policy developments on the EU level. One main results is that, while the methodology appears sufficiently developed, there is still a considerable shortage of empirical data. This is because past research has focused mainly on particular types of soil degradation (mainly erosion), and on particular impacts (mainly those on agriculture). As a consequence, comprehensive assessments of the cost of soil degradation are few and far between, and many aspects of soil degradation still escape an economic valuation.

1. Introduction

Soil performs a multitude of functions that are essential to human life. Apart from providing food, biomass and raw materials and serving as a habitat and gene pool, soil also performs storing, filtering and transformation, as well as social and cultural functions. In this way, soil plays an integral part in the regulation of natural and socio-economic processes that are necessary for human survival. Because soil forms the basis of many different human activities, it also has a significant economic value. However, this "fundamental" value of soil proves difficult to quantify.

Intensive agriculture, land consumption for building, the contamination of soil through pollutant emissions and changing climatic conditions are but a few of the man-made pressures on soil. While healthy soil can withstand these pressures to a certain degree, the combination and the extent of the stresses has resulted in a slow, but widespread, degradation of soils in many parts of Europe.

In reaction to this, the European Commission is currently preparing a thematic strategy on soil protection. Possible elements of this thematic strategy can be found in the Commission Communication "Towards a Thematic Strategy for Soil Protection" (European Commission 2002). The publication of the thematic strategy was originally scheduled for June 2004, but is now expected for the end of 2004.¹

In addition, the European Commission introduced a system for ex-ante impact assessment of all major policy proposals. The impact assessments are supposed to ensure that economic, social and environmental effects of new policy initiatives are duly taken into account. There has been a tendency to give particular emphasis to the costs and benefits of policy proposals.² Against this background, the European Commission has commissioned a study on assessing economic impacts of soil degradation.

¹ This article is based on intermediate results of the research project „Assessing Economic Impacts of Soil Degradation, which is financed by the European Commission, DG Environment. It will be completed in July 2004.

² Along these lines, Article 147 of the Amsterdam Treaty, demands that "In preparing its policy on the environment, the Community shall take account of the potential benefits and costs of action or lack of action". It is manifest e.g. in the development of the groundwater daughter directive, which was supported by an economic study, or in the demand of the 2004 Spring European Council, to prepare a cost benefit analysis of different climate policy options.

2. Approach and Methods

The physical, chemical and biological effects of soil degradation on other media of the environment, ecosystems and human populations have been researched to some degree. With the possible exception of organic matter loss or the loss of soil biodiversity, the causes, mechanisms and impacts of the different soil degradation processes are understood sufficiently well, and can be assessed and measured. However, the economic impacts that soil degradation imposes both on the users of soil and on society as a whole have received little emphasis so far.

In order to take stock of the available economic empirical evidence on soil degradation, the authors have conducted a survey of the existing studies and a review of the relevant literature that has quantified in economic terms the impact of different types of soil degradation. This is done for the eight types of soil degradation identified by the European Commission, i.e. erosion, contamination (local and diffuse), salinisation, decline in soil organic matter, soil sealing, floods and landslides, compaction and loss of soil biodiversity.

The literature survey provides a review of the main concepts, methods and issues that are discussed in the soil-scientific and economic literature. Main aspects that are addressed in the review are the following:

- Derivation and description of a typology of soil degradation, including basic concepts to describe the dynamics of soil degradation processes, as well as the identification and description of the most important types of soil degradation;
- Description of possible indicators to describe soil degradation processes and their impacts (both environmental and socio-economic), as well as an overview of possible data sources;
- Derivation and description of the methodology for assessing the economic impacts of soil degradation trends in Europe, including the identification of relevant cost categories and methods to estimate the impacts and related costs;
- Overview of existing empirical estimates assessing the costs of soil degradation, which includes mainly agronomic and other economic studies from European and other industrialised countries.

The literature survey has looked at a variety of impacts associated with soil degradation, both direct and indirect. Whereas direct impacts include, for example, yield losses due to compaction or salinisation, indirect economic impacts comprise e.g. losses in the value of agricultural land affected by erosion, losses in residential property values due to contamination, or the cost of replacing eroded nutrients through fertilisation. Likewise, the analysis considers on-site as well as off-site effects of soil degradation. And, along with the use values of soil (e.g. for farming, forestry, recreation or housing), it also addresses non-use values (or patrimonial values).

A special category are the indirect use values of soil, these include the ecosystem services provided by soil and their economic role. The concept of ecosystem services has recently attracted much attention in ecological economic research. Soil is an integral part of many ecosystems and natural processes, including the regulation of the natural water cycle, nutrient cycling, the creation and absorption of biomass, the sustenance of biodiversity, and the natural carbon, sulphur and nitrogen cycles. These diverse functions are of enormous importance for human survival and for economic activity. However, so far, the economic value of these ecosystem services has not been assessed comprehensively.

This is due to several factors. First of all, the precise functioning and the interdependencies of ecosystems are still only partly understood. Partly as a consequence, the ecosystem services provided by soil are often taken for granted, and are only discovered when they are lost. Secondly, ecosystem services have the characteristics of a public good: the services provided by one ecosystem are dispensable as long as there are other ecosystems providing the similar services. Also, the benefits that soil supplies through the ecosystem services may accrue to spatially or temporally remote users, e.g. in the case of climate regulation.

Yet the evaluation of soil degradation is characterised by a variety of different methods and approaches. This is also due to the fact that not all soil functions are of direct and measurable

economic relevance: Besides its use for agriculture, horticulture and forestry soil also has ecological, cultural and aesthetic functions, for instance as an archive of human and natural history, or by fulfilling spiritual or religious functions. While such functions cannot be adequately measured in economic terms, they contribute to the value of soil nonetheless.

Analytically, the economic valuation of soil degradation can be understood as a change in the value of soil quality. Soil degradation is a deterioration of soil quality, i.e. a loss of soil functions. Consequently, the process of valuing soil quality can be described as moving from the soil functions (which are described by ecology) to the uses of soil (which are at the interface between ecology and economics) to the valuation of these uses (which is an economic task).

To assess the impacts of soil degradation, the damage costs can be divided into five categories:

- the on-site (private) costs of damage suffered as a consequence of soil degradation, such as yield losses that farmers incur if the agricultural productivity of soil has been reduced through erosion, compaction or other degradation processes. These costs are denoted in the figure as PC;
- the on-site private cost of restoration and repair measures to restore degradation or to prevent further erosion. This includes, for example, the cost of additional fertiliser input, or the cost of measures to restore the physical soil structure of compacted soils. This category is labelled RC;
- the off-site (social) costs of soil degradation, which are suffered by other parties. One example is the cost of damages caused by floods and landslides. It also includes the value of foregone ecosystem services, that are affected by soil degradation. These costs are denoted SC;
- the defensive costs incurred in order to mitigate or limit the off-site impacts of soil degradation. This includes e.g. the cost of dredging canals in order to remove eroded sediment, or the cost of conservation measures to prevent landslides. These costs are abbreviated as DC;
- the non-user costs that accrue to the individuals that do not use the soil, but are nonetheless distressed by its degradation. This measures impacts on the non-use values attached to soil, e.g. the patrimonial value of preserving soil for future generations. These costs are captured as NC.

Figure 1 below gives a schematic overview of these cost categories.

3. Results and Discussion

The literature survey covers a total of 60 empirical economic studies. The majority of these studies come from North America and Australia (20 and 19, respectively); 12 studies cover European sites. About half of the studies assess the lost (agricultural) output caused by soil degradation, five studies make use of contingent valuation, and nine apply the hedonic pricing method. In addition, a number of studies have assessed restoration cost of degraded soils, e.g. the cost of replacing lost nutrients.

Of the different types of soil degradation that are identified by the Commission, erosion is the phenomenon that is covered most extensively in the empirical economic literature. Of the 60 studies included in the survey, 43 focus on erosion, six on contamination, and 11 on other types of soil degradation. The economic effects of compaction, biodiversity loss and loss of organic matter are covered only in occasional studies, or are not quantified at all.

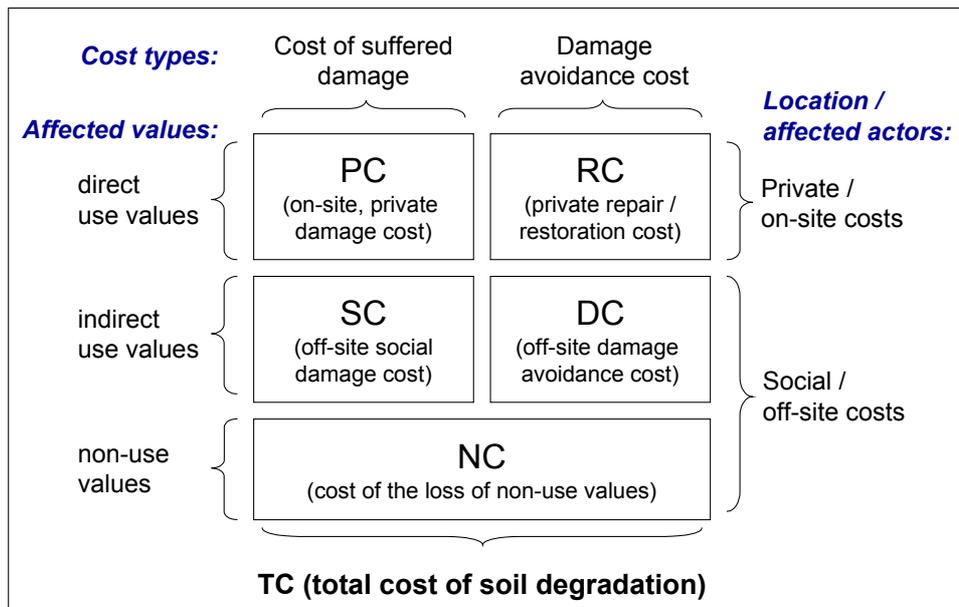


Figure 1: Overview of different cost components

Several studies provide evidence that the total cost of soil degradation is indeed significant. Estimates of the total, nation-wide or state-wide cost from Australia, Canada, New Mexico and Spain have produced results between € 200 million and € 1.9 billion per year (expressed in 1999 €). While these numbers should not be compared directly, they illustrate that the potential economic impact of soil degradation can reach a significant size, even if viewed on a macroeconomic scale.

In the case of soil erosion, the off-site (or social) costs represent a significant part of the total costs, often exceeding the on-site impact through reduced yield losses. For the UK, estimates of these impacts range from € 50 million to € 224 million per annum (Evans 1996, Pretty et al. 2000). For the US, single estimates range as high as US\$ 9 billion per annum (Ribaud 1989).

The majority of empirical estimates centre on the direct, on-site effects that soil degradation has on agriculture and forestry. By contrast, the effect of soil degradation on indirect uses of soil has received less attention. In particular, the impact of soil degradation on the ecosystem services provided by soil has been quantified only occasionally. Yet, the limited evidence that is available indicates that ecosystem services indeed form a significant part of the impacts of soil degradation.

- The FAO Soil Biodiversity Portal (FAO, undated) provides some estimates of the value of ecosystem services provided by soil, based on a study by Pimentel (1997). They estimate the value of waste recycling, soil formation, nitrogen fixation, bioremediation of chemical pollution, biotechnology (genetic resources), biological pest control, pollination and the support of wild animals and ecotourism. The worldwide economic value of these services is estimated at US\$ 1.542 billion, of which 49 percent is due to waste recycling alone. However, the study does not provide any evidence how these numbers are affected by soil degradation.
- Balmford et al. (2002) assess the economic value of different ecosystems. For the cases they investigate, they find that the economic gains of converting ecosystems to human use are actually negative. For the case of a Canadian wetland, the total economic value actually decreased by almost 60% as a consequence of conversion (from US\$ 8,800 to US\$ 3,700 / ha / y). For other ecosystems, they arrived at comparable results. The reason for this is that the loss of the non-marketed services provided by the ecosystems is not outweighed by the marginal benefits of conversion. The finding holds despite the fact that some ecosystem services, such as nutrient cycling and the provision of cultural values, were not considered due to a lack of data.

4. Conclusions

In terms of methodology, the economic assessment of soil degradation faces the challenge to adequately represent the different facets and impacts of soil degradation, while at the same time reducing complexity so far as to make an economic assessment possible. While the available economic methods appear sufficiently developed to meet this challenge, data availability is clearly limited.

On the whole, comprehensive assessments of the costs of soil degradation are few and far between. Particular aspects have received some attention in the past: for example, there is considerable evidence of the economic impacts of erosion on agricultural productivity, mainly stemming from agronomic studies conducted in the US. However, on the whole, the available evidence is very limited, meaning that the multifunctionality of soil and the complexity of soil degradation are not captured sufficiently.

Some of the biggest uncertainties in the economic valuation of soil degradation are still related to the ecosystem services that soil provides. One reason for this is that the interactions between soil and other environmental media are only partly understood. As the limited empirical evidence indicates that ecosystem services could form a significant part of soil's value, this uncertainty is especially troubling. Other obvious limitations apply to the non-use values (or patrimonial values) attached to soil, e.g. through its spiritual, cultural or historical functions. Assessments of these are virtually non-existent.

This means that a comprehensive, reliable and robust estimate of the costs of soil degradation will be very hard to arrive at now or in the near future. The divergence of results from different studies demonstrates that subjective interpretations and assumptions do influence the outcomes of the analysis considerably.

However, despite these apparent limitations, the assessment of economic impacts of soil degradation can provide an important input for finding the appropriate policy response to soil degrading activities. Several studies provide evidence that the total cost of soil degradation can be significant enough to justify a more proactive approach to soil protection. This is especially true if one considers that a large part of soil's value has not even been assessed, and given the fact that soil is essentially non-renewable.

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Concept for a regional, process based estimation of diffuse substance inputs into groundwater – a contribution to the implementation of the EU Water Framework Directive

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Abstract: A method was developed which allows quantifying the regional potential of diffuse nitrogen input into groundwater. It is a process based approach which considers the kinds of land use of agriculture, forest and urban areas. The core is the estimation of a denitrification rate of the covering soils by a Michaelis-Menten-Kinetics (e.g. after Wendland, 1992) for agriculturally used areas. It is shown, that the estimation of the mineral nitrogen pool in the soil can be done by using generally available data. The input of total nitrogen atmospheric deposition is determined from the data base of the Critical Loads and Critical Levels method (Gauger et al., 2002). The agricultural N input is determined by the N-Balance-Method. For forested areas the denitrification is estimated by means of the parameters Ntotal-deposition, N-immobilization, N-netto-uptake and a temperature dependent denitrification factor (after Nagel & Gregor, 1999). The denitrification of urban areas is considered by using the Ntotal-deposition, N-mobilization from organic matter and a constant denitrification amount (after Hirt, 2002; Gebel & Grunewald, 2002). The result is the potential nitrogen amount in the seepage water which is converted into potential nitrogen concentration in seepage water using the amount of groundwater recharge. The method was applied within the scope of a pilot project at two groundwater body areas in Saxony (Germany). The transfer of the method for an implementation of the EU Water Framework Directive (WFD) in Saxony is currently carried out.

1. Introduction

The implementation of the EU - Water Framework Directive (WFD) regarding diffuse substance inputs into groundwater requires methods which allow an area-wide estimation. In a first step the groundwater bodies were assessed by the environmental agencies with regard to the kind and degree of pollution. Groundwater bodies exceeding the target values were marked as "endangered". For these bodies a more detailed investigation must be carried out, and suitable methods must be developed. In the German Federal State Saxony, the main risk of diffuse pollution consists in pollution by nitrogen. Therefore a method has been developed which allows calculating the nitrogen input into the groundwater in consideration of agricultural and air born nitrogen inputs as well as different kinds of land use and denitrification rates of different soil types. The basis is an investigation of a number of known methods which represent the current state-of-the-art. These methods are not completely suitable regarding the requirements of implementation of WFD. Therefore selected methods have been adapted and combined. The bases are procedures by Wendland (1992) und Gebel & Grunewald (2002) for agriculturally used areas, Nagel & Gregor (1999) for forest and by Hirt (2002) for urban areas.

The new method was created for an efficient application in regional scale. The method is GIS-processing (ARC-INFO) in combination with SQL-queries and Visual Basic. The new method has been applied at two groundwater bodies in Saxony. An extensive verification and a sensitivity analysis have been carried out.

The behaviour of nitrogen in soil is known and described in textbooks e.g. Scheffer & Schachtschabel (1992). About 95 % of nitrogen in soil is bound in organic matter and immobile, whereas 5 % is ammonia and nitrate. About 5 % can be mobilised during one year. Ammonia has small importance

and can be neglected. The most important transformation processes are mineralisation and nitrification. The denitrification in soils is a heterotrophic process in the most cases. The variation of denitrification rates have a wide range, i.e. 15 to 50 % of the yearly applied N-fertilizer. Denitrification means a reduction of water pollution in particular for groundwater. The denitrification loss amounts to about 0 in forest to 29 kgN/ha*a in carbon rich soils. The algorithms of the method are described in the following.

1. Calculation of N-leaching for agriculturally used areas

The considered components of the N-balance are shown in Fig. 1. Basis of the method is the agricultural N-balance (Eq. 1). In Germany this balance is available for agriculturally used areas which are aggregated to settlement areas. The balance is calculated by agricultural agencies.

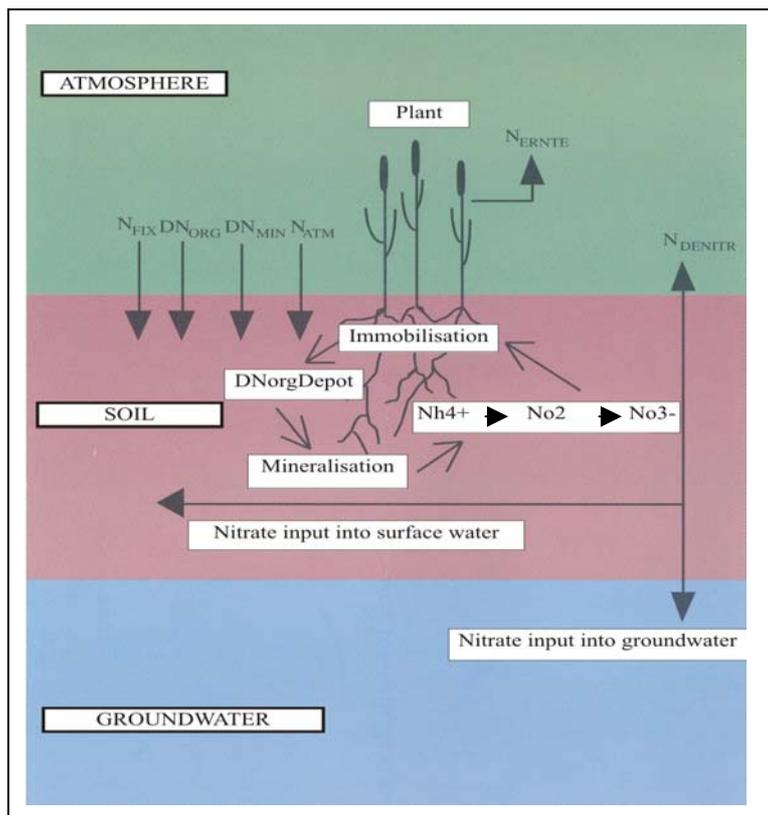


Figure 1: N-input and output as well as nitrogen transformation in soil (LfUG, 1998) with mineral fertilizer (DN_{min}), organic fertilizer (DN_{org}), legume N-fixation (N_{fix}), atmospheric deposition (N_{atm}), removal by harvesting (N_{ernte}), loss by denitrification (N_{denitr}).

The following calculation scheme is used:

$$\begin{aligned}
 \text{N-Input:} & \quad \text{Min. fertilizing (DNmin)} \\
 & \quad + \text{Organic fertilizing (DNorg)} \\
 & \quad + \text{Legume N-fixation (Nfix)} \\
 & \quad + \text{Atmospherical deposition (Natm)} \\
 \text{N-Loss:} & \quad - \text{Harvest (Nernte)} \\
 \text{N-Saldo (N-excess):} & \quad = \text{N-Input} - \text{N-Output} \qquad \qquad \qquad (\text{Eq. 1})
 \end{aligned}$$

From this a mean saldo for agriculturally used areas of the groundwater body is calculated. The atmospherical deposition is usually not included in the agricultural N-balance. For this investigation the N-deposition from Gauger et al. (2002) is used.

Whereas the model input for the N-balance: DN_{min}, DN_{org}, N_{atm}, N_{fix} and N_{ernte} can be accepted as known, the denitrification which is the most important transformation process is hard to determine. This is due to the sensitivity of the process with regard to several transient soil parameters. The denitrification is favoured by:

- The existence of readily biogradable organic substances as energy supplier,
- High soil moisture,
- High soil temperature (15-50°C),
- The existence of nitrate in soil
- Lack of oxygen in soil air and seepage water

Therefore, the main issue of the following explanations shall be the quantification of the denitrification process. The principle of inclusion of denitrification is shown in Fig. 2.

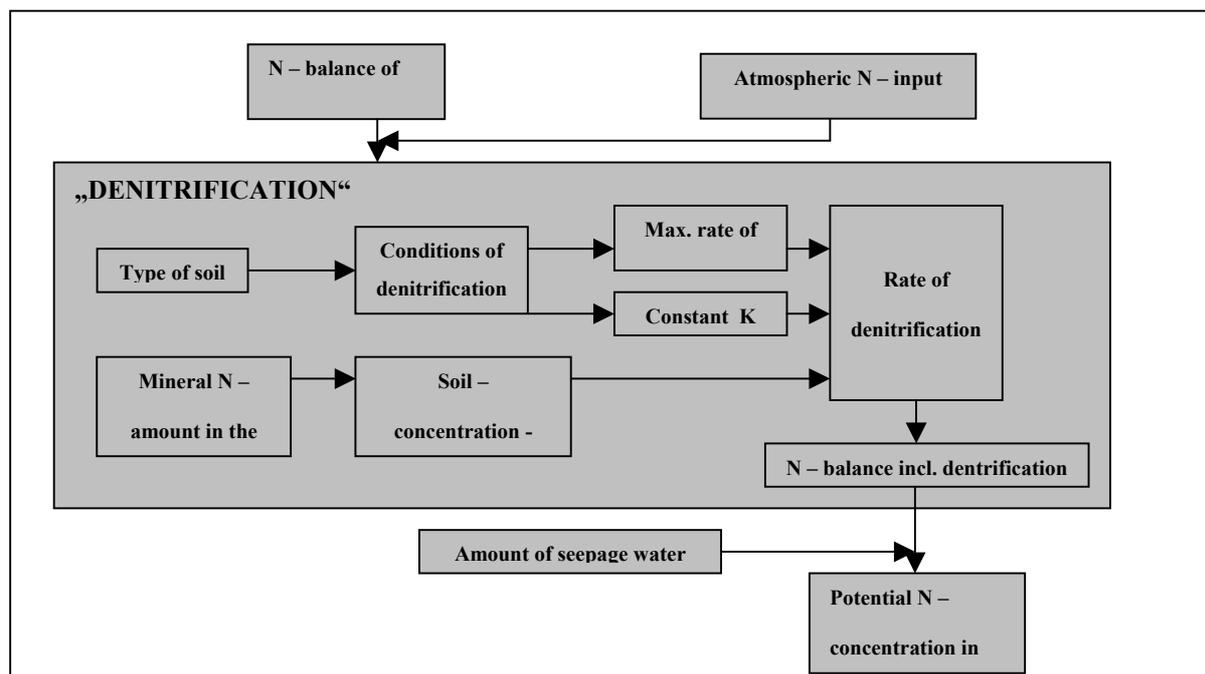


Figure 2: Principle procedure for estimation of the denitrification rate, the saldo and the potential seepage water concentration.

Based on the agricultural N-balance the "additional information on denitrification" is calculated depending on the conditions of denitrification and the mineral N amount of the soil. This is carried out depending on the distribution of the soil types within the groundwater body. The conditions of denitrification are estimated in three classes on base of the saxonian soil map (1: 200.000) by the environmental agency. From that an "N-balance including denitrification" (N_{deni-Saldo}) is calculated. By multiplying with groundwater recharge, potential seepage water concentration (c_{Nsiwa}) can be calculated.

The estimation of the denitrification rate is carried out process-based with the Monod kinetic (after Wendland, 1992). This allowed getting a differentiated calculation depending on the above mentioned favouring criteria for denitrification. But the challenge is the lack of input data required for a state-wide application. In particular area-wide data of N_{min} are not available. The calculation equation is shown in Eq. 2

$$N_{denitr} = D_{max} * ((N_{min}/7.5)/(K+N_{min}/7.5)) \quad [\text{kgN/ha/a}] \quad (\text{Eq. 2})$$

with N_{denitr} = denitrification rate [kgN/ha/a]; D_{max} = maximal denitrification rate depending on soil type [kgN/ha/a]; N_{min} = mineral nitrogen in soil [kgN/ha*a]; K = Monod constant

(by an assumed soil mass of $7.5 \cdot 10^6$ kg/ha)

To solve the problem N_{min} must be estimated from available information. It can be done by the following equation (Eq. 3)

$$N_{min} = DN_{min} + 0.3 DN_{org} + N_{atm} + N_{minDEPOT} \quad (\text{Eq. 3})$$

N_{min} is calculated as follows: The data for DN_{min} and DN_{org} are obtainable from the agricultural agencies (Agrarstatistik) and can be aggregated for the groundwater bodies. N_{atm} can be extracted from the digital data base of the German Umweltbundesamt (UBA; German Environment Agency) (Gauger et al., 2002) which is nation-wide available. $N_{minDepot}$ can be calculated, after LfUG (1998):

$$N_{minDepot} = (0.625 \cdot DN_{org} + 0.95 \cdot N_{ges}) \cdot (1 + FKT_{min}/4) / 100 \quad [\text{kgN/ha/a}] \quad (\text{Eq. 4})$$

N_{ges} is the organic nitrogen in soil. $N_{minDEPOT}$ is the part of the organic nitrogen which is mineralised every year. Simplifying can be assumed equilibrium of mineralisation, i.e. the mineralisation is in mean constant for several years. Further N_{ges} is assumed as constant (recommendation of the agricultural agency: 5000 kgN/ha*a) and representativ for the investigation area.

Because the DN_{org} amount is also very small compared with N_{ges} it can be neglected. With that N_{depot} can be calculated as follows:

$$N_{minDEPOT} = (0.95 \cdot N_{ges} \cdot ((1 + FKT_{min})/4)) / 100 \quad (\text{Eq. 5})$$

The FKT_{min} value is insensitive, so it can be estimated and set as a constant value. The calculation of N-saldo in consideration of denitrification (N_{denitr} -Saldo) is carried out as follows:

$$N_{denitr}\text{-Saldo} = N\text{-Saldo} - N_{denitr} \quad [\text{kgN/ha/a}] \quad (\text{Eq. 6})$$

After that the potential seepage water concentration (c_{Nsiwa}) can be calculated by

$$N_{denitr}\text{-Saldo} \cdot 100 / \text{Seepage water amount [l/m}^2] = c_{Nsiwa} \text{ [mg/l]} \quad (\text{Eq. 7})$$

This calculated concentration is used for the assessment of the risk potential for groundwater pollution.

3. Calculation algorithm for forests

The algorithm for forests is derived from the Critical Loads Concept (Nagel & Gregor, 1999). The calculation is started with the atmospheric deposition minus N-uptake and N-immobilisation. Both parameters are site specific. The N-uptake depends on yield class and immobilisation on yearly mean of temperature at the site. The denitrification factor depends on the group of soil kind. The following calculation scheme is used:

<i>N-Input:</i>	Atmospherical deposition in forest (N_{atm})
<i>N-Loss:</i>	- N-uptake
	- N-immobilisation
	- Denitrification factor (f_{deni}) * ($N_{atm} - N\text{-uptake} - N\text{-immobilisation}$)
<i>N-Saldo:</i>	= $N_{denitr}\text{-Saldo} \cdot 100$
	/ $SiwaMenge \text{ [l/m}^2]$

$$\text{Pot. N-concentration: } = cN_{\text{Siwa}} \quad (\text{Eq. 8})$$

This calculated concentration is used for the assessment of the risk potential for groundwater pollution.

4. Calculation algorithm for urban areas

The data base for settlements is to a very large extent insufficient. Therefore a very simple algorithm after Gebel & Grunewald (2002) has been chosen. The calculation starts with the atmospheric deposition and an N-delivery of the soil is added and a denitrification rate is subtracted. For that lumped parameters are used, i.e. the N-delivery and the denitrification rate are constant. The following calculation scheme is used:

$$\begin{aligned} N\text{-Input:} & \quad \text{Atmospheric deposition (open area)} \\ & \quad + \text{N-delivery of the soil} \\ N\text{-Loss:} & \quad - \text{Denitrification rate in soil} \\ N\text{-Saldo:} & \quad = N_{\text{denitr-Saldo}} * 100 \\ & \quad / \text{SiwaMenge [l/m}^2\text{]} \\ \text{Pot. N-concentration:} & \quad = cN_{\text{Siwa}} \quad (\text{Eq. 9}) \end{aligned}$$

This calculated concentration is used for the assessment of the risk potential for groundwater pollution.

5. Conclusions

The application of the method is carried out by using SQL and Visual Basic to create the GIS-based database and all the attribute table data inside of MICROSOFT Access. With it an efficient tool was created which enables a time saving area-wide investigation. The method was applied at two groundwater bodies in the German Federal State Saxony. The required data are either area-wide available or can be obtained from public information systems. A verification of the method at a test plot is not possible because of missing comparison data. But a first checking step was carried out by applying the method at several lysimeters with various soil types. With that an acceptable fit of calculated and measured results has been obtained. A sensitivity analysis has been carried out to find insensitiv parameters. It can be shown, that the uncertain parameters have no or just low sensitivity.

The main restrictions are admittedly the lacks of area-wide data and the very small time budget for both the development and the application of the method within the WFD. The latter makes it impossible to initiate data preprocessing of non public data bases. On this account several simplifications have to be made. Nevertheless the important balance components are considered. The developed method is suitable for description of the status-quo. For that the method allows the estimation of comprehensible and reliable results. Changes in the system e.g. accumulation or degradation of organic matter or dynamic processes can not be described. For these objectives a more sophisticated method with higher process relation must be applied.

The method appears to be a suitable tool for a state-wide estimation of N-leaching potentials and possible groundwater related risks for diffuse pollution. Under acceptance of certain uncertainties a way was shown, how an area-differentiated determination of the denitrification can be carried out in spite of data lacks.

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POSTERS

Determining parameters of dual-permeability model from laboratory column experiment

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1. Introduction

Uncertainty in modeling unsaturated water flow and solute transport in vadose zone has several different sources. One of them, and probably the most significant one, is related to the determination of model parameters. Besides the more direct experimental approaches, the method of inverse modeling is recently more and more often used to determine the flow and transport parameters. Parameter estimation of flow and transport properties by inverse modeling is an attractive option to classical methods, especially in case of soils where preferential flow occurs. By definition, solving an inverse problem implies that unknown causes are determined based on observation of their effects.

Important role during formulation of inverse problem play selection of data sets, identifiability, well-posedness and uniqueness. An increase of likelihood of non-uniqueness and instability in the inverse solution may be caused by larger number of optimized parameters in the van Genuchten parametric model (Russo et al., 1991). Jacques et al. (2002) indicated that combining numerical solutions of the governing flow and transport equations with inverse optimization algorithm is a promising approach for parameter identification provided that detailed measurements are available. Estimation of soil hydraulic parameters in combination with solute transport parameters from laboratory column experiment yields advantage of more precise and quick data collection, but produce complications with up-scaling of the determined properties to the field scale. Abassi et al. (2003) carried out two-step sequential optimization in which they first estimated soil hydraulic parameters followed by the estimation of the solute transport parameters. It allowed them to include additional parameters to the optimization process.

High quality of data as well as correct choice of parameters to optimization is crucial. Regardless of uncertainty, which cannot be avoided from many reasons, it is recommendable to verify correctness of the results by repeated optimization from different initial parameter estimates.

2. Materials and methods

To check the potential of inverse modeling, laboratory experiments on large undisturbed soil sample were conducted. The soil under study - coarse sandy loam (Cambisol) - represents highly heterogeneous soil with wide particle size distribution and is known to exhibit preferential flow effects (Cislérova et al., 2002b). The dimensions of the sample were 25 cm in height and 18.9 cm diameter. The laboratory infiltration-outflow experiments with automated data acquisition (Snehota et al., 2002), involving measurement of a tracer breakthrough curve, were performed. The unsaturated flow through the sample was established by means of a disk tension infiltrometer. In the presented case, constant suction pressure head of 1cm was applied to the top of the sample. The bottom boundary condition was a seepage face. Solution of Rhodamin tracer (initial concentration 20 mg/l) replaced clean water supply in time 1.5 hours after start of the infiltration-outflow experiment. The weight of the sample, as well as pressure head and inflow and outflow rates of water and tracer were recorded.

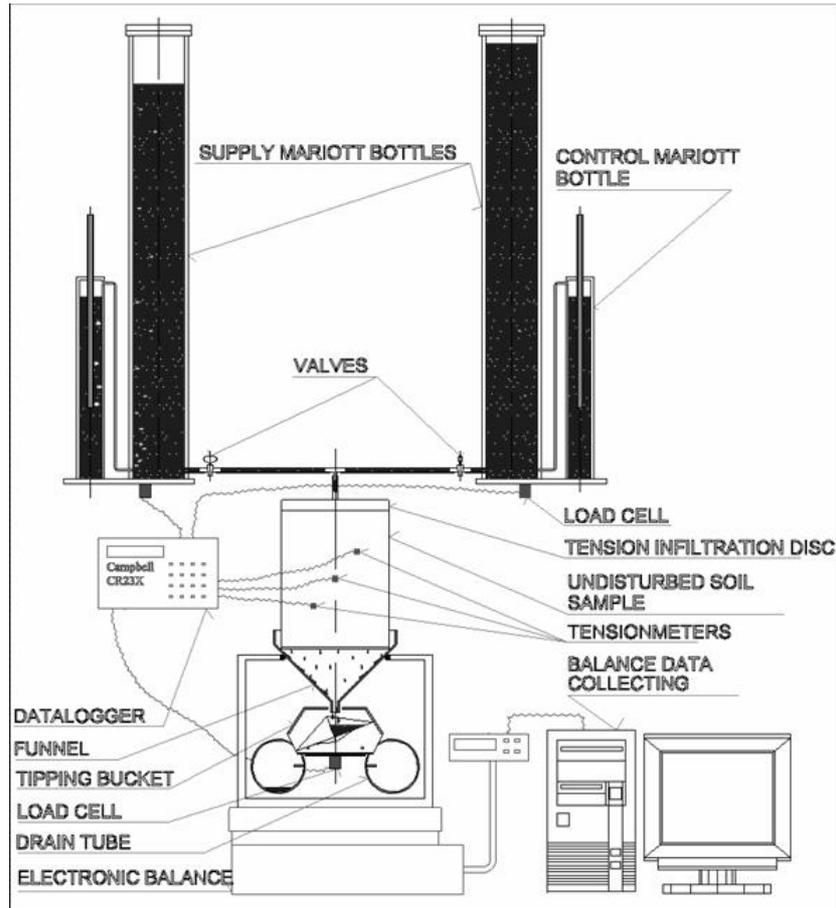


Figure 1: Complete scheme of the experimental set-up

Solving the associated inverse problem for hydraulic and transport parameters ensued. The S_1D_DUAL code, developed from the earlier single-permeability program HYDRUS 5 (Vogel et al. 1996), was used as a one dimensional dual-permeability forward simulator. In S_1D_Dual, the pore space is represented by a dual-permeability system (Vogel et al. 2000), consisting of the matrix flow domain (MFD) and the preferential flow domain (PFD), in which the PFD occupies a certain fraction of the bulk soil. Model is based on the Richards' equation and hydraulic properties of unsaturated flow are approximated using van Genuchten's expressions.

Solute transport is solved in the model by means of coupled convection-dispersion equations

$$\frac{\partial}{\partial t} R_m \theta_m c_m + \frac{\partial}{\partial z} q_m c_m - \frac{\partial}{\partial z} \left(\theta_m D_m \frac{\partial}{\partial z} c_m \right) + \theta_m \mu_m c_m = + \frac{\Gamma_s}{w_m} \quad (1)$$

$$\frac{\partial}{\partial t} R_f \theta_f c_f + \frac{\partial}{\partial z} q_f c_f - \frac{\partial}{\partial z} \left(\theta_f D_f \frac{\partial}{\partial z} c_f \right) + \theta_f \mu_f c_f = - \frac{\Gamma_s}{w_f} \quad (2)$$

where c is the solute concentration [M/L^3], D is the hydrodynamic dispersion coefficient [L^2/T], and q is the Darcy flux [L/T]. R the dimensionless retardation factor and Γ_s is the solute mass transfer term [$M/(L^3T)$] evaluated as

$$\Gamma_s = \Gamma_w c_i + \alpha_s (c_f - c_m) \quad (3)$$

where α_s [1/T] is first-order solute mass transfer coefficient.

The parameter estimator PEST (Waterloo Hydrogeologic), based on the Levenberg-Marquardt algorithm, was used for non-linear optimization. The flow and transport parameters were optimized in least-square sense.

3. Results and Discussion

Initial values of hydraulic parameters were derived from measured soil-water retention relationships in combination with information obtained from CT measured porosity distribution according to Cislerova et al. (2002a). Four parameters were optimized (n , K_s , D , K_d). Two most sensitive soil hydraulic parameters n and K_s (in MFD) were chosen (Table 1). Moreover solute two transport parameters: dispersivity (D) and distribution coefficient for equilibrium sorption (K_d) were optimized.

Table 1: Values of hydraulic parameters in the S_{1D} Dual

domain	θ_r (-)	θ_s (-)	α (1/cm)	n (-)	K_s (cm/h)
MFD	0.030	0.396	0.080	1.7077*	5.721*
PFD	0.045	0.822	0.145	2.995	170.000

marked values were optimized

Optimal values of transport parameters were found to be: $D = 4.13$ and $K_d = 3.5 \cdot 10^{-4}$, respectively. Determined parameters allow very good description of flow and transport processes in soil sample (see Fig. 3).

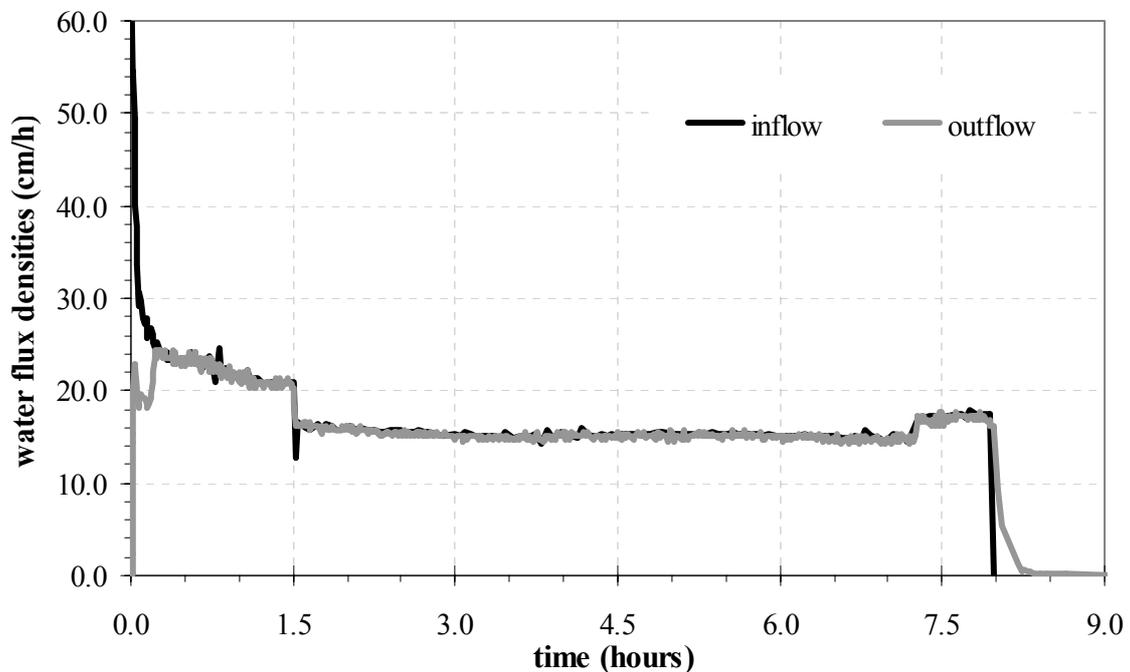


Figure 2: Time behavior of inflow and outflow

Measured water flux densities (Figure 2) provided excellent information to identify processes and its uncertainties during experimental run. There are several stages of the inflow/outflow record which are so far poorly physically unexplained and thus difficult to approximate by the model (see the first 90 minutes and at the end of experiment). Simulated inflow or outflow rates (not displayed) were approximately straight lines near the steady state value in the Figure 2 (between 1.5 and 8 hours). This corresponds very well with measured data except for the slightly elevated part at the end of experiment (near 8 hours).

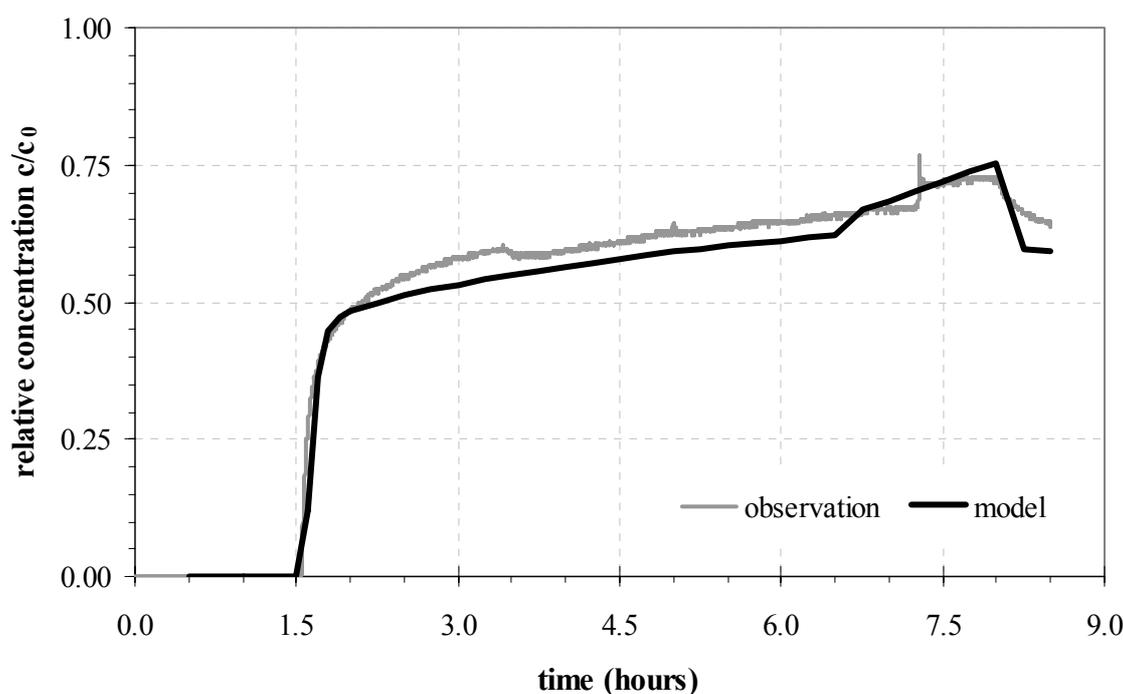


Figure 3: Comparison of outflow relative concentrations during experiment

Some of the above mentioned optimization problems as well as problems associated with flow instabilities are demonstrated in Figure 3. Deviations and oscillations in measured concentration can be caused by air entrapment effects etc. Some errors belong to experimental setup respectively. Therefore partial mismatch between measured and simulated outflow concentration is inevitable.

4. Conclusions

Several optimization scenarios resulting from different combination of observed data in the objective function were tested and compared. It is shown that the inclusion of additional type of data in the objective function (in our case the tracer breakthrough curve information) can help to recognize measurement errors and significantly reduce its impact on optimization. An important feature of the discussed inverse modeling approach is the combination of two different parametric models: the one used for the water flow parameters (related to the Richards' equation) and the one used for the solute transport parameters (related to the advection-dispersion equation).

The results of comprehensive sensitivity analysis confirmed suitability of the inverse modeling approach for estimation of soil hydraulic and solute transport properties of the heterogeneous soil in question.

5. Acknowledgements

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Pesticide transport through tropical soils

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1. Introduction

The evident lack of reliable field data leads to significant uncertainty in identification of maximum contaminant levels for pesticides. The U.S. Environmental Protection Agency (EPA) issues maximum limits in groundwater systems for each pesticide, however this database must be updated since new chemicals are being introduced on market every year. The chemical and physical interactions between soils and applied pesticides pose such a complex behavior that cannot be easily modified to different site conditions. Moreover, the synergy effect when applying more pesticides at a time is unknown. Therefore, values of coefficients in literature should be viewed only as rough guide. From all of this follows that both the field-scale and laboratory experiments are crucially needed for improved insight into pesticide transport in soils.

An increasing evidence of organic pollutant residues detected in groundwater aquifers has intensified research of contaminant transport through vadose zone. Pesticides which are widely used in agriculture and are considered as less mobile compounds with relatively small persistency have been in recent years found in groundwater wells in Oahu, Hawaii State. With a development of new chemical compounds, the Hawaii Department of Agriculture (HDOA) is supposed to register new pesticides, which are already EPA-registered, according to their leachability under field conditions. Their transport behavior is not so far properly described in tropical soils. To test these new chemicals, an extensive field and laboratory experiments were carried out at University of Hawaii.

It has been shown by previous studies that not every field-scale or laboratory experiments obey the traditional Richards' and the convective-dispersion equations. The instability of the onward wetting front in soils has been proven to occur under various conditions. This phenomenon has a direct influence on infiltration, drainage and specifically on solute transport. Preferential flow through interaggregate pores of highly aggregated soils or induced by a spatial heterogeneity has been recently reported (Booltink and Bouma, 1991; Lennartz *et al.*, 1999; Vervoort *et al.*, 1999; Vogel *et al.*, 2000). Hawaii Oxisol is also assumed to produce significant preferential flow patterns due to water movement through the interaggregate pores (Balasubramanian *et al.*, 1973; Rao *et al.*, 1974).

The project is aimed at evaluating the movement of four herbicides (atrazine, s - metolachlor, imazaquin, and sulfometuron methyl), two fungicides (trifloxystrobin and metalaxyl) and an insecticide (imidacloprid) at five sites representing diverse hydrogeologic environments. Three of the five sites were located on Oahu (Kunia, Poamoho and Waimanalo research station), one was located on Maui (at Kula experimental station) and the last site was established on Kauai (at Mana district). All studied chemicals have been already registered by the EPA for use in crop or residential areas. However, some of these chemicals have not been used in Hawaii yet.

2. Material and Methods

Five sites were established on three Hawaii islands, representing distinct climatic, soil-chemical and hydrological conditions. All studied soils have developed from volcanic activity.

2.1 Irrigation setup

The irrigation layout of four plots was designed at each site. Two rectangles were used for herbicides (marked as 1H and 3H) and the other two for insecticide and fungicide (with labels 2F and 4F). Hence, each site had duplicate plots for herbicides and insecticides/fungicides. The dimension of each rectangle was 20 by 30 feet (6.1 m x 9.1 m). The set-up on Maui differed in shape and also in number of nozzles, because the spatial conditions did not allow building typical irrigation layout. The irrigation consisted of PVC pipes with varied diameters, pressure reducing valve, screen filter, 18 (20 at the Kula site) adjustable aerial sprinklers distributed on the boundaries of plots and a digital unit, which controlled the duration and switching on/off of the irrigation. The irrigation intensity slightly differed among all five sites (12.8-13.7 mm/hour and 20.3 mm/hour for the Kula site) depending on the pressure in the irrigation system. Uniformity tests of the irrigation were carried out repeatedly to obtain even distribution of irrigated water over plots. Since the local weather conditions (and thus rainfall distribution) for each site varied, the irrigation system delivered amount of water equivalent to about 70% of potential evaporation. This amount of water resembles the agriculture needs when growing sugarcane or corn in the areas of interest.

2.2 Site instrumentation

Prior to chemical application, each site was sufficiently equipped with measurement devices. The time-domain reflectometry (TDR) probes, manual and automated tensiometers were installed for the inspection of water flow dynamics.

At four sites (Kunia, Poamoho, Waimanalo and Mana), two pits were dug and the TDR probes were inserted horizontally at 30, 60 and 90 cm below the soil surface. The TDR probes consisted of three parallel rods in a plane, with a rod length of 20 cm, a rod diameter of 3 mm, and a spacing of 3 cm between the rods. The experimental site in Kula received also two TDR pits, but TDR probes were inserted to 25 cm, 51 cm and 76 cm respectively. The values of volumetric water content were measured continuously during the field experiment in frequency of one week by Trace system digital receiver (Soilmoisture©).

Similarly to TDR installation, two nests with automated tensiometers (Soilmoisture©) were installed on two plots (herbicide and fungicide/insecticide) at each site. Three depths of the position of the porous cups were the same for four sites (Kunia, Waimanalo and Mana): 30 cm, 60 and 90 cm below the surface. At the Poamoho site, only two couples of automated tensiometers were installed into 30 and 60 cm depth complemented with manual tensiometers serving the 90 cm depth. Installation depths at the Kula site were 25 cm, 51 cm and 76 cm. The diameter of automated tensiometer was 1.5 cm. All automated tensiometers were fitted with the pressure transducers Honeywell 236PC15GW for continuous soil tension recordings.

Twelve manual tensiometers were regularly installed at four sites of interest (Kunia, Poamoho, Waimanalo and Mana). The depths of tensiometer porous cups corresponded with the depths of TDR installation, i.e.: 30, 60 and 90 cm below the soil surface. Only two manually-controlled tensiometers nests were installed at Kula. Again, installation depths at the Kula site were only 25 cm, 51 cm and 76 cm below the soil surface. The manual tensiometers were in the design of Soil Measurement Systems and consisted of a ceramic cup, PVC plastic body and acrylic extension. The tensiometers were sealed with rubber septums at the top to allow measurements. The manual tensiometers had a diameter of 1.5 cm. The values of suction head were measured continuously during the field experiment in frequency of one week by digital unit Soil Moisture Systems-Tensimeter™.

All automatically collected data were stored in data loggers (Campbell, 21X, CR10X, CR10X-M), the measured values were read approximately every 10 – 15 minutes depending on memory capacity.

2.3 Chemical application

Each plot was raked before the application and treated as a bare soil. Prior to pesticide spraying, potassium bromide tracer was applied on all four plots on each site at rate of 0.033 kg/ha. All herbicides were mixed in a container and applied using a hand-held CO₂- pressurized sprayer (3 m boom with six nozzles). Similarly, fungicides and insecticides were applied together to adjacent plot at the same location. Each plot was split into two spraying walks along its longer dimension. To enhance the leaching process of applied pesticides, the irrigation system was run for one hour. A 2 cm layer of straw was spread over each plot within hours after pesticide application to limit erosion and surface sealing and also to prevent photodegradation of the pesticides.

2.4 Soil-chemical sampling

The migration of pesticide and tracer was monitored over the period of 16 weeks. The sampling of disturbed soil was carried out with bucket auger. The depth of sampling increased with time propagation. First sampling day occurred one day after chemical application and consisted of only one soil sample taken from the first 15 cm below the surface. The soil sample from depth of 2.1 m was recovered at the last sampling date, i.e. at week 16. The depth increment was 30 cm, except for the first 30 cm below the soil surface, where two samples were taken. Three boreholes on each plot were drilled to obtain the soil sample. Then, the sample was homogenized in clean heavy duty plastic bag. Afterwards, sample was put into a glass jar, taken into transport cooler and consequently all samples were stored in a cooler room in order to cease the degradation process.

2.5 Measurement of unsaturated conductivity

The measurements of the unsaturated hydraulic conductivity as a function of applied pressure head were undertaken at each site with tension infiltrometer. Measurements were performed in the vicinity of application plots. The applied pressure heads at the soil surface were -20, -12, -6, -3, -1 and 0 cm. The measurements at zero pressure head should represent saturated water movement, thus the saturated hydraulic conductivity can be evaluated. In addition, the hydraulic conductivity function at specified pressure heads were measured at linear transect along the application plots. The measurements were carried out with the same measurement technique but the measurement device was different in diameter of contact area. The selected applied pressure heads at the soil surface were -10, -5, -2 and 0 cm.

2.6 Laboratory experiments

The degradation study, batch sorption tests and measurements of retention properties of soils were performed in the laboratory. Beside these experiments pH, organic carbon content and background concentrations were determined. Additionally, an undisturbed soil monolith from the Poamoho site will be set up in the laboratory and a tension infiltrometer will be used to deliver water to the top of the column. The water flow through aggregated Oxisol will be investigated under different applied pressure heads to confirm and quantitatively evaluate the expected preferential flow effects.

3. Results and Discussion

Fig. 1 is an example of soil water tension fluctuation during the period of one month as a result of natural (rain and drying) processes and irrigation water applied. The tensiometer installed at 30 cm below the surface shows quite fast response to artificial irrigation. The upward water movement due to enhanced evaporation-induced gradient is also clearly reflected in Fig. 1.

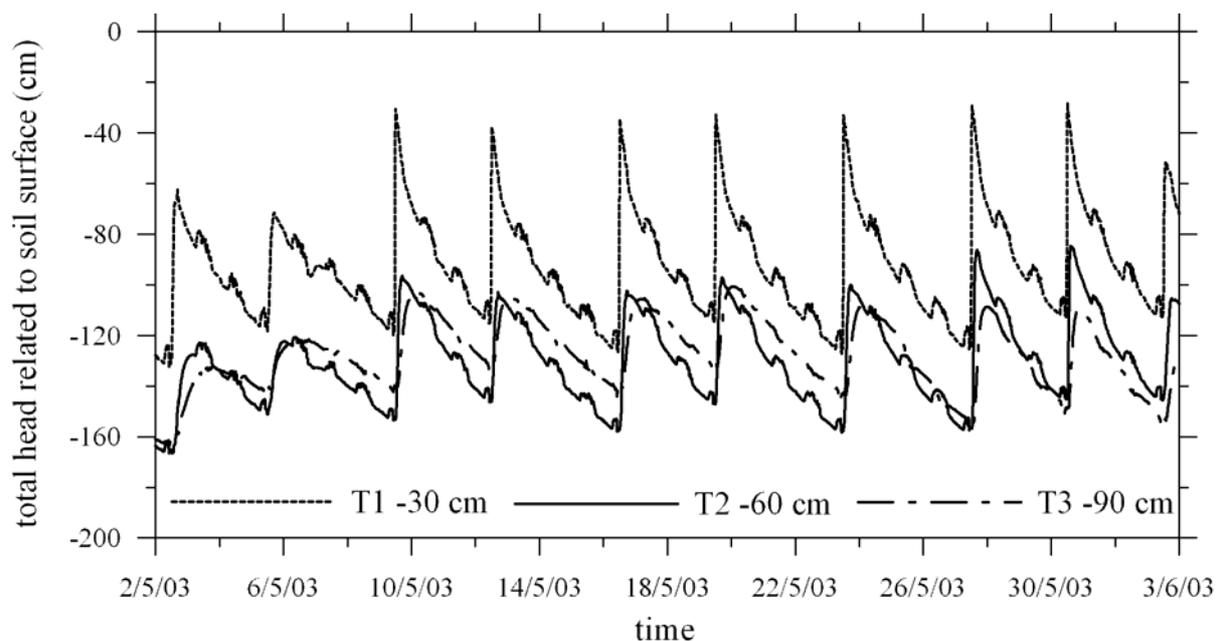


Figure 1: Total head development at three depths is depicted during May, 2003 at Kunia.

The space-time development of bromide field content at the Kunia site is depicted in Fig. 2. Also, the standard deviations calculated from four disturbed samples are shown. It is clearly evident that the sampling depths over the whole experimental course were significantly underestimated. As a consequence, the bromide peaks in the soil profile are not sufficiently covered by sampling. The results suggest some sorption of the bromide tracer near the soil surface. In addition, an apparent uncertainty in the bromide concentrations can be seen from the plotted standard deviations in Fig. 2. This can be attributed to experimental difficulties (uncertainties) of sampling procedure and analytical concentration determination, spatial variability of the soil, and/or few soil samples. The calculated standard deviation near the surface even exceeded the respective measured bromide concentration and thus are not plotted.

From the evidence of relatively deep penetration of bromide tracer in response to natural rainfall and irrigation, it has been previously concluded that nonequilibrium transport in the aggregated Oxisol takes place (Gavenda *et al.*, 1996). This conclusion indicates the necessity to apply a numerical model capable of simulating water movement and solute transport through the preferential pathways.

4. Conclusions

One-dimensional, dual-permeability model S 1D Dual (similar to the model presented by Vogel *et al.*, 2000) based on Richards' and advection-dispersion equation was chosen for modeling the pesticide fate and mobility during the field experiment. This numerical code allows for dividing the porous media into two mutually communicating pore systems. The influence of nonequilibrium (either physical or chemical) transport will be examined. The modeling efforts will be conducted using (i) independently determined parameters, and (ii) estimated transport parameters by inverse method from laboratory column displacement experiment.

Additional focus will be dedicated to quantitative risk assessment of the measured pesticide penetration. Final results and recommendations should address the issue of the potential leaching of applied chemicals, thus the state authority would be able to properly register the respective pesticide product or restrict the use of compounds that leach easily or persist for a long period of time.

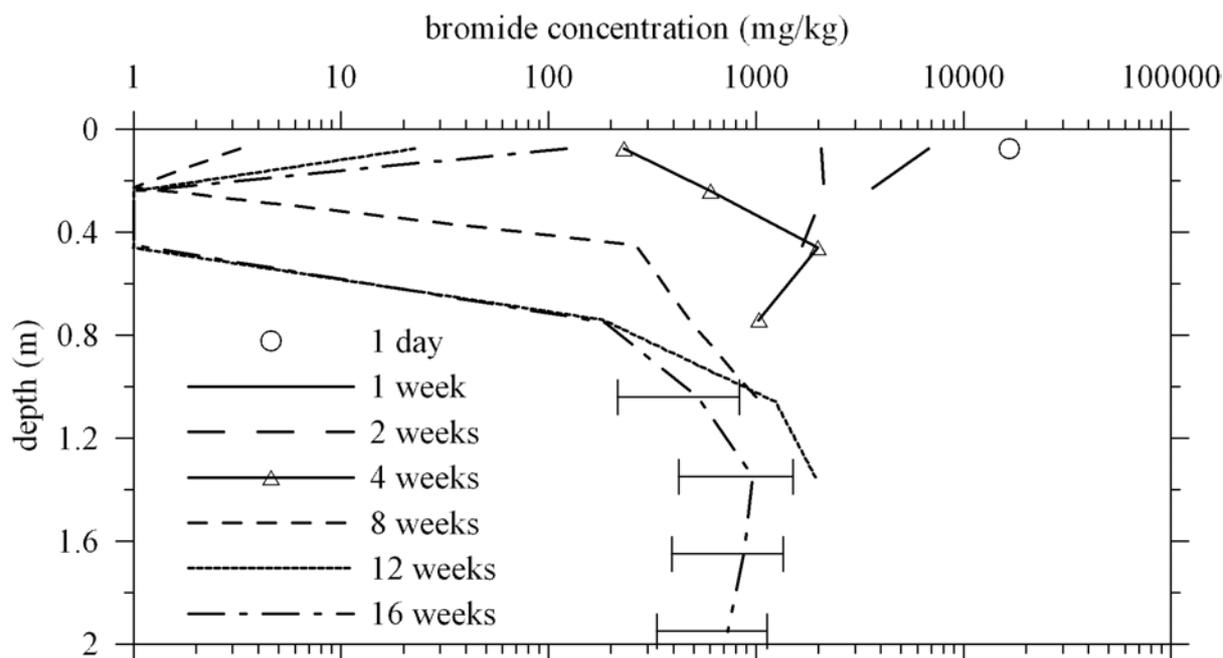


Figure 2: Measured bromide profile during 16 weeks of field experiment at Kunia. The standard deviations at the last sampling event are marked by error bars.

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Integrated soil and water protection against diffuse pollution (SOWA)

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Abstract: SOWA pulls together scientific knowledge from various disciplines such as soil science, soil chemistry, soil physics, hydrogeology, water resources, agriculture, atmospheric deposition of pollutants, environmental analysis and engineering as well as management and remediation of contaminated soil and groundwater. SOWA provides a multidisciplinary forum for the identification of research needs and strategies for integrated soil and water protection. The research needs and strategies are identified in five thematic working groups which focus on the different aspects of integrated soil and water protection: Inventory of priority compounds and trends, screening and monitoring tools at different scales, biogeochemical and physical processes, heterogeneity and scale issues in soil and groundwater, management options for large scale soil and water pollution incl. environmental economics / socio-economic issues.

1 Scope and original objectives

Soil and water pollution is a result of population growth and technological development. Industrial development has brought prosperity to millions of people, but has also left a legacy of environmental damage that continues to impact natural resources and ultimately the human well being. A wide range of man-made chemicals designed for use in industry, agriculture, pest control, consumer goods, and emissions from the combustion of fossil fuels are the main sources for diffuse pollution. Within the water cycle, soils act as the key zone for storage, filtration and transport of water and associated pollutants. Water sooner or later interacts with soil and / or sediments, and this interaction determines the quality of groundwater, surface waters and finally drinking water. If the accumulation of pollutants exceeds the buffer capacity, then soils or sediments can become the source of diffuse pollution of adjacent compartments such as for groundwater and surface waters..

In the EU Soil Thematic Strategy (DG ENV - *Towards a Thematic Strategy for Soil Protection*, COM(2002), 179 final), diffuse pollution is itemised as main threat to the soil by direct or either indirect pollution due to the disposal/use of sewage sludge, incineration sludge, compost and pesticides.

Experience shows that large scale remediation of diffuse pollution is economically not feasible and that soil contamination is not reversible at a reasonably time scale. The motivation of SOWA is the protection of soil as the most active resource in the hydro- and biosphere and as the essential environmental compartment for food production and finally human health.

The main goal of SOWA is to identify scientific questions which address the most relevant research needs for integrated protection of soil and water resources in future.

This includes the evaluation of especially large scale soil pollution which will potentially damage important soil functions (such as the buffering, filtering, transformation capacity) and the soil ecology.

In addition, SOWA identifies tools and procedures for low cost screening and contaminant analysis, soil characterisation methods, and management of soil/water contamination in Europe.

With workshops, publications, newsletters, conference presentations, and press releases SOWA increases the awareness of the risks of diffuse soil pollution, which pose a risk of long-term contamination of the water cycle.

2 Scientific approach

The approach of SOWA is to identify from a scientific point of view the risks arising from the continuous pressure of man onto soils leading to damage of crucial soil functions such as:

- Base for ecosystem quality, sustainable land use and safe food production
- Filter for drinking water
- Key compartment in global biogeochemical cycles (carbon, nitrogen, water...)
- Sink/source for anthropogenic and natural pollutants,

SOWA focuses on the physico-chemical multifunctionality of the soil, on long-term vs. short term issues, and on European/global and local dimensions.

SOWA is organised as a “think tank“ in five thematic working groups:

- Inventory: Identification of priority compound classes such as persistent organic pollutants and heavy metals
- Biogeochemical and physical processes
- Heterogeneity and scale issues in soil and groundwater
- Screening and monitoring tools at different scales
- Management options for large scale soil and water pollution including environmental economics and socio-economic issues.

The SOWA-partners come from nine different disciplines (hydrogeology, environmental chemistry, geophysics, soil physics, soil science, water resources, agriculture, environmental engineering, analytical chemistry). With this multidisciplinary thematic structure, the project is able to cover the different aspects of soil and water protection. In addition, SOWA invites internationally leading experts to meetings and workshops in order to integrate additional expertise.

3 Main results/output

Contamination of our natural resources, such as atmosphere, water, and eventually soil have received much attention in the past decades. The awareness that contamination requires management and remediation has been a major incentive for several EU framework programmes. During the past decade, limits to the funds available for active remediation have become increasingly recognised and they steered environmental policies from remedial technologies into the direction of appropriate management and prevention of contamination. The latter approach - where key concepts in risk analysis are biological availability and mobility of contaminants - is not only a change in perception, but also a change in nuances to be considered. Both of these key concepts are to a large degree controlled by the concentration of contaminants in the gaseous and aqueous phases of soil and water resources and the atmosphere.

Inventory

During the last decades, large amounts of different chemicals were released to the environment through industrial waste, agricultural practice (including manure and sewage sludge applications) and via wastewater treatment plant effluent discharges. This contamination can have a critical impact in the ecosystem due to their strong activity at low doses. According to an inventory of priority compound classes, persistent organic pollutants (POPs) have been identified to exhibit potentially harmful effects to man and the environment. In addition to being persistent, POPs are typically lipophilic and therefore bioaccumulative, and toxic (pbt: persistent, bioaccumulative and toxic). Actually, a second wave of pollutants, the so-called emerging contaminants are suspicious of causing adverse effects in both humans and wildlife. In addition, intermediates and end-products of the chemical and pharmaceutical (incl. veterinary) industry have to be mentioned. One of the key issues with emerging contaminants is that although few of them have been recently subject to legislation, many potential pollutants are not fully recognised and as a consequence no routine monitoring

programmes exists. One of the key issues is the evaluation of risks of such non-regulated chemicals that are currently being detected in the environment.

Processes

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

Scales

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

Monitoring

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

Management

Presently diffuse pollution of soils and water is tackled by sectorial approaches. Water or soil protection usually focus on their specific domains and do not sufficiently coordinate their efforts. The sectorial focus is also reflected in the legislative basis of these activities. Different laws relate to soil and water protection. As chemicals are cycling in the environment between different compartments, problems in one compartment often are caused by activities in another compartment. The nitrate problem in groundwater is a perfect example. Even severe overfertilisation of agricultural land does create a serious problem for soil quality. Excessive nitrate loads can be quite rapidly removed through the uptake by plants which are subsequently harvested or via leaching. In waters on the other hand, as pointed out before, nitrate is a pollutant of prime concern. Even rather low fractions of the nitrogen fluxes which are turned over in agricultural cropping systems can already cause very serious pollution if they are exported into water bodies. Problems of this kind demonstrate that a holistic, integrative approach is desperately needed. Fig. 1 shows the interconnections between the environmental

compartments, animals/cattle, and humans and the pressure pathways of pollutant inputs. The arrows and especially the crosspoints of arrows indicate the problem zones for ecosystem management, which have to be tackled together in an integrative way.

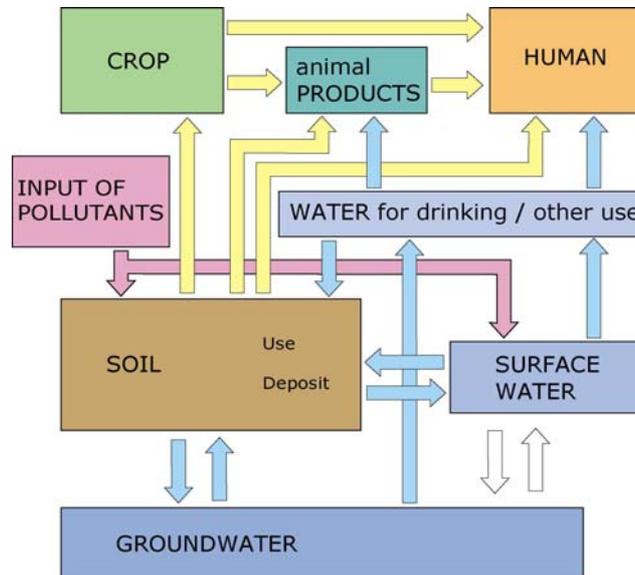


Figure 1: Pollutant fluxes into and out of soil, groundwater and surface water compartments, as well as pathways to human, animal and crop plant receptors.

Subcritical water remediation of soils contaminated with TNT, RDX and HMX

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1. Introduction

Explosives-contaminated soil and groundwater at manufacturing and packaging sites poses environmental risks. Waste disposal procedures and destruction of out-of-date munitions have extended the problem. Owing to their stability and mobility in the soil, explosive substances and their degradation products can also leach to the groundwater. TNT (2,4,6-trinitrotoluene) is the most widely spread soil contaminant [1]. RDX (1,3,5-trinitro-1,3,5-triazacyclohexane) and HMX (1,3,5,7-tetranitro-1,3,5,7-tetrazacyclooctane) appear in 44% and 27% of the samples, respectively. The present study is concerned with the application of subcritical water extraction as a practical method for clean-up of contaminated soil.

At present, incineration is the most widely used method for the remediation of explosives-contaminated soil. Soil is fed into the primary combustion chamber of a rotary kiln (~700°C), where most of the explosive residues are destroyed or vaporised [1]. The combustible or toxic vapour is treated further in a second combustion chamber that operates at a higher temperature (>1500°C). The final product of incineration is ash.

Lately, supercritical fluids have been used for the decontamination of significant quantities of soils contaminated with several hundred ppm levels of polycyclic aromatic hydrocarbons (PAHs) and pesticides [2]. In these studies, dynamic (flowing) water was used to remove the contaminants from the soil. In another study, supercritical CO₂ has been used to extract polychlorinated biphenyls from river sediment [3]. Additionally, herbicides and pesticides such as trifluralin (R,R,R-trifluoro-2,6-dinitro-N,N-dipropyl-p-toluidine) and pendimethalin (N-(1-ethylpropyl)-2,6-dinitro-3,4-xylidine) have been degraded in soil using water above 150°C. Treatment of the pesticide/herbicide contaminated soil is interesting because of the structural similarity of these chemicals to the aforementioned explosives. Therefore, the degradation of TNT, RDX, and HMX on naturally contaminated soils at the lab scale and pilot scale is examined, using only pure water and the contaminated soils placed in heated stainless steel vessels under static (no water flow) conditions.

2. Experimental Section

Soils: The TNT-contaminated soil was obtained from a Ministry of Defense site in the United Kingdom and contained 12 wt % (120000 ppm) of TNT but no significant levels of other explosives. The soil was used without any pre-treatment for the 2-g and 40-g lab-scale experiments. The RDX/HMX (3200 ppm/750 ppm respectively) contaminated soil was obtained from a military storage site in Texas (U.S.A.), and was carefully sieved to remove rocks and sticks and properly mixed to ensure homogeneity. Aqueous solutions taken from both soils showed a pH of ~7. The concentrations of the explosives on both soils were determined after analysis (see below) of each homogenized bulk soil sample.

Subcritical Water Apparatus: Two laboratory (5-mL) and one pilot (8-L) reactors were used for the subcritical water treatment studies. The 5 mL reactors for the 2-g samples were constructed from 316 stainless steel pipe with national pipe threads and end caps sealed with Teflon tape. These reactors were loaded with 2 g of soil and 2 mL of HPLC-grade water (which had been purged with nitrogen to remove dissolved oxygen) allowing ca. 1.5 mL of headspace in the reactor. The 75 mL reactor was constructed from 316 stainless steel tubing with welded conversion fittings to 1 in. (2.54 cm) “Swagelok” tubing fittings. “Swagelok” caps were used to seal both ends. Each run used 40 g of soil and 40 mL of water.

A batch of the smaller reactors (5 mL) was mechanically shaken for 5 minutes, to ensure good mixing of the soil with the water, and then placed upright in the oven. The oven was then heated rapidly (>25°C/minute) to 25°C above the prescribed temperature and the control was then reset to the target temperature. This procedure was aimed to counteract the effect of the heat capacity of the cell and contents. Zero time was taken to be when the oven had reached the experimental temperature. Thermal measurements showed that the run-up time within a cell, to reach 95% of the set increase, was 9 minutes. Experiments were performed at selected oven temperatures in the range 50 – 250°C. After the experiment was completed, the reactors were allowed to cool to room temperature. For analysis of the residual explosives, the contents of each reaction cell were centrifuged for 10 minutes to achieve maximum soil-water separation.

The pilot-scale reactor was constructed of 304 stainless steel, had a tubular shape and capacity of ca. 8.2 L. It was wrapped with six 620W heat tapes, which were controlled in three zones with separate thermocouples. For maximum safety, the reactor was constructed with 2 pressure relief valves, in case the pressure exceeded the safety limits [4]. Venting was controlled by a manual shut-off valve mounted in the vent line. Two pilot-scale runs (one with each soil) were performed using 4 kg of soil and 4 L of tapwater with the reactor in the horizontal position. One additional run was performed using 6 kg of soil and ca. 2 kg of water with the reactor in the vertical position.

(Safety note: All static (nonflowing) reaction vessels must contain sufficient headspace so that the pressure inside the vessel is controlled by the steam/liquid equilibrium. A reaction vessel must never be used full since the pressures could exceed the safety limits. For these studies ca. 20% (or more) of the reactors’ volume was left empty to ensure adequate headspace).

Analysis. All treated and untreated soils and residual wastewaters of every experiment were analyzed using EPA method 8330 [1]. Concentrations of the explosives on both site derived soils and from the prepared standards were determined following sonication of 2 g samples in the presence of acetonitrile (HPLC grade) for 18 hours, as required for analysis by EPA SW846 method 8330. An HPLC separation was performed by isocratic elution with 82/18 water/isopropanol for TNT and 95/5 water/isopropanol for HMX and RDX. Solvent programming from 85/15 water/methanol to 100% methanol was used to obtain higher resolution in order to analyze selected samples for intermediate products. The flow rate of the eluents was set at 1 mL/min for all analyses. A Waters HPLC system (model 2487) equipped with a 20 µL sample loop and a “Nova-Pak” C-18 HPLC column was used. Peaks were identified and quantified from the injection of standard explosives (Supelco, PA, USA). Atrazine was used as the internal standard. Calibration curves were obtained by preparing TNT, RDX and HMX solutions of known concentrations, 1, 5, 10, 20, 50 and 100 ppm.

Bacterial Toxicity – TCLP test (EPA Method 1311) . The bacterial toxicity of the soils and the wastewaters was determined by “Microtox” tests. These tests were performed on water leachates of the treated and untreated soils and on the process wastewaters by a commercial laboratory (AquaTox Research, Inc., Syracuse, NY) using the luminescent bacteria *Vibrio fischeri* [5,6].

The TCLP test (Toxicity Characteristic Leaching Procedure) is an official EPA test designed to determine the mobility of both organic and inorganic analytes present in liquid, solid and multiphase wastes. This test was performed on the treated TNT and RDX/HMX soils. The soil leachates that were obtained with the TCLP method, were analyzed using the same HPLC procedure that was also used in our main experimental analysis.

3. Results

Lab-Scale. Tests with the pilot-scale reactor showed a heating rate of ca. 2.5°C/min, therefore the lab-scale tests were performed by programming the GC oven temperature from 25°C to 275°C at 2.5°C/min. A batch of identical reactor cells (each containing the same amounts of soil and water) were placed in the oven, and individual cells were removed as the oven reached various temperatures so that the remaining explosives in the soil and water at each temperature could be determined.

As shown in Figure 1, TNT began to show significant degradation in the reactor heated to 200°C, and almost complete degradation in the reactor heated to 250°C [4]. RDX and HMX-contaminated soils showed a similar behaviour, although significant degradation started at somewhat lower temperatures than for TNT. All three explosives were completely degraded (based on analysis of both the treated soils and the wastewaters) when the reactors were allowed to reach 275°C. The results in Figure 1 also indicate that the largest quantities of non degraded contaminants were found in the soil phase rather than in the wastewater, possibly because solvated molecules (that had not degraded) repartitioned to the soil upon cooling, or because the explosives degraded rapidly once solvation in the water occurred. Another explanation is that the degradation reactions could occur mainly on the soil surface, although rapid degradation of the explosives spiked into water (with no soil present) also occurs, demonstrating that the soil matrix is not necessary for the degradation reactions.

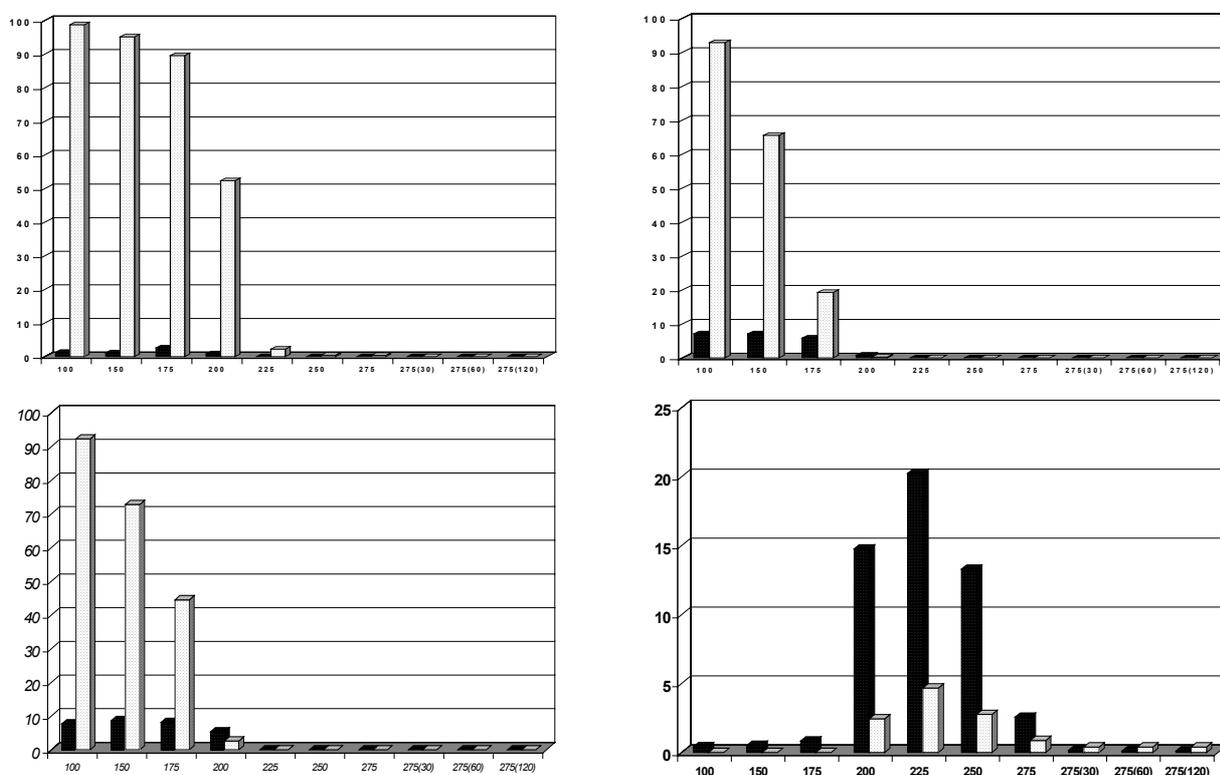


Figure 1: Degradation of TNT (top left), RDX (top right), and HMX (bottom left) on contaminated soils exposed to subcritical water at different temperatures (x axis). White bars indicate the remaining percentage of the contaminant on the soil fraction whereas black bars indicate the remaining percentage on the water fraction. Heating was performed from 25 to 275°C at 2.5°C/min to resemble the behaviour of the pilot-scale reaction vessel. Reaction vessels were removed from the oven when the temperature shown on the figure was reached. The formation of a TNT degradation product is presented in the bottom right diagram.

Based on these results, additional lab-scale tests were performed using reactors heated to follow the experimental behaviour of the pilot-scale unit, i.e., (heating rate of 2.5°C/min) and then held at 275°C for 1 h. Additionally, since the amount of TNT-contaminated soil available at the 12 wt % contamination level was not enough for pilot-scale tests, triplicate degradation experiments were

performed using 40 g of the 12 wt % TNT soil and 40 mL of water in the 75-mL lab-scale reaction vessel to provide the necessary quantities of treated soil for the biological tests. The results of these lab-scale experiments (triplicate reactions at each condition) performed to mimic the pilot-scale experiments are shown in Table 1. For the 2-g samples, all of the TNT, RDX, and HMX (and the TNT intermediate product discussed below) were degraded below their analytical detection limits of 1 ppm in the water and the soil. Similarly, triplicate runs of 40-g subsets of the 12 wt % TNT soil (with 40 mL water) resulted in only low ppm levels of TNT remaining in the soil and wastewater (Table 1).

Intermediate Degradation Products. The HPLC analysis of the treated TNT soil and wastewater indicated the presence of an intermediate reaction product. As shown in Figure 1 (bottom right diagram) its appearance begins at about 200°C and its maximum concentration reaching ca. 24% of the total TNT concentration (assuming the UV response factor for the degradation product is the same as for TNT) in the reactor heated to 225°C [4]. However, the concentration of this product dropped rapidly as the reaction temperatures were increased and disappeared when the reactor was heated to 275°C for 60 min or longer. Only one significant degradation product from the RDX/HMX-contaminated soil was observed, with a maximum concentration (assuming the same HPLC/UV response factor as RDX) of ca. 20% of the total RDX concentration in the reactor heated to 150°C (data not shown). This intermediate product quickly disappeared as the reactors were exposed to higher temperatures. It is important to note that these intermediate products are not the toxic reaction products such as the nitroso derivatives of RDX (based on the lack of detectable mono-, di-, and trinitroso derivatives of TNT, RDX, and HMX compared to the HPLC/UV behavior of standard compounds). Indeed, the fact that this treatment process uses no added oxidant (note that the water for the lab-scale experiments was purged to remove dissolved oxygen), renders formation of the nitroso-derivatives unlikely, in comparison to approaches such as supercritical water oxidation, bioremediation and wet air oxidation, that primarily yield oxidation products [7-12].

Table 1: Lab- and Pilot-Scale Degradation of TNT, HMX and RDX on Historically Contaminated Soils with Subcritical Water at 275°C for 1 h.

Sample size	Sample	Original concn, mg/kg±SD ^a	soil	Concentration after treatment, mg/kg±SD ^b		Total % degraded ^c
				wastewater		
2 g	TNT	120000±10000	<1	<1		>99.99
40 g	TNT	120000±10000	2±2	4±3		99.99
4 kg	TNT	12000±1000	<1	5±2		99.96
2 g	RDX	3200±400	<1	<1		>99.9
	HMX	750±140	<1	<1		>99.7
4 kg	RDX	3200±400	<1	2±1		99.9
	HMX	750±140	1±1	15±3		97.9
6 kg	RDX	3200±400	<1	4±1		99.9
	HMX	750±140	2±1	27±4		97.3

(a) Original concentrations were based on the analysis of eight 2-g subsamples of each homogenized bulk soil sample. (b) Standard deviations are based on triplicate degradation runs for the 2- and 40-g runs and on the extraction and analysis of triplicate soil and water subsamples from the pilot-scale runs. (c) Total percent degraded was determined by comparing the sum of the explosive concentrations in the wastewater plus their concentrations in the soil after treatment to the concentrations in the soil before treatment.

The elution of the major products on reverse-phase HPLC prior to the primary explosives indicates that they are more polar than the primary explosives, as might be consistent with attack by hydroxyl radicals of the aromatic ring. It is known that TNT biotransforms readily under both aerobic and anaerobic conditions to give aminodinitrotoluenes, and the resulting amines biotransform to give several other products, including ate, azoxy, acetyl and phenolic derivatives, leaving the aromatic ring intact. The colour of the wastewater at certain temperatures indicates the presence of some Meisenheimer complexes. These complexes, initiated by hydride ion attack on the TNT ring, can also be formed during TNT biodegradation [13].

Pilot Scale: Based on the results of the lab-scale studies, the pilot-scale remediations were performed on both TNT and RDX/HMX-contaminated soils by heating the reaction cell to 275°C (requiring ca. 100 min) and holding the temperature for 1 h. As shown in Table 1, the results from the pilot-scale runs agreed well with those of the lab-scale tests, and overall degradation of the TNT, RDX, and HMX was very high [4]. Final concentrations of the explosives in the soils were sufficient to meet typical target treatment values of a few ppm [e.g., 30-50 ppm in ref 14] suggested for these explosives. The wastewaters appear sufficiently clean to allow reuse for additional soil treatments, since each wastewater had only traces of residual explosives, a pH of ca. 6.5, and no odor of ammonia.

Bacterial Toxicity: "Microtox" assays demonstrated an EC₅₀ of 0.0006% for untreated TNT soil and 1.0% for treated TNT soil. This means a 1700-fold reduction in the toxicity of soil leachates from the 12 wt % TNT-contaminated soil after subcritical water treatment. The RDX/HMX soil leachates also showed a 35-fold reduction in toxicity (EC₅₀ of 0.03% for untreated soil and 1.0% for treated soil). Bacterial toxicity of the wastewaters was also low (EC₅₀ values of 3% and 52% for the HMX/RDX and TNT wastewaters, respectively). In contrast, it is noteworthy that wet air oxidation studies of TNT-contaminated waters can result in increased in bacteria toxicity [15-17]. Finally, the EPA TCLP test (Toxicity Characteristic Leaching Procedure) showed no detectable levels of explosives in the soils leachates after treatment.

4. Conclusions

The treatment of contaminated soils with subcritical water offers several advantages. No additives, catalysts, or oxidants, of any kind are used. The equipment is very simple i.e., only a pressure vessel constructed of stainless steel, a source of water, and a source of heat are required. No pumping system is needed to maintain the system pressure, since pressure is automatically controlled by the steam/water equilibrium. Based on the conditions used in our study, estimates based on the approach of Montero et al. predict a cost of \$125/ton whereas treatment using composting requires \$125-210/ton, supercritical water oxidation requires \$220-650/ton and treatment by incineration costs ca. \$1600/ton [18]. The pilot-scale tests described in this study were performed under rather severe conditions (275°C, which results in 60 bar pressure). However, it is possible to lower the costs and safety demands by treating soils in lower temperature and pressures. For example, lab-scale studies carried out at 150°C show that 98% degradation of TNT on the 12% contaminated soil could be achieved with ca. 6 h of treatment, greater than 99% destruction of HMX can be achieved in 2-3 h, and ca. 95% destruction of RDX could be achieved with 3½ h of treatment [4].

With the appropriate safety precautions, the process poses no safety risks since, (after the reactors are filled), operation is performed from a remote location by simply turning on the power to the unit at the beginning of the run and off after the run is completed. Compared to supercritical water oxidation corrosion is minimized, since we have lower temperatures and no reactive additives are used. Additionally, the low contaminant concentrations found in the process wastewaters show that a single volume of water can be used to treat multiple soil samples. The soil extracts obtained at any stage of the process can be easily and quickly analysed, which means that this method allows for trouble-free monitoring of the treatment stages. Most importantly, our initial studies demonstrate that very highly contaminated soils can be rapidly treated to very low contaminant levels, without the production of more toxic by-products.

5. Acknowledgements

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The BERRILUR Initiative: a Basque integrated and strategic project in soil and groundwater issues

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1. Introduction

Strategic research projects: are projects to extend knowledge in strategic areas of the agents operating within the Basque network of technology and innovation, in accordance with integration of science and technology, which may be pluri-annual; plans for high-level training at the most suitable centres and institutions; with a high content of international co-operation.

BERRILUR is the strategic project in soil and groundwater issues financed by the Department of Industry, Commerce and Tourism and the Department of Environment and Land planning (Basque Government).

Main aim of the project: To generate, develop, complement and incorporate the knowledge needed to solve the problem of soil pollution which must be inevitably faced by the society (in general) and the industrial sector (in particular) of the Basque Country (Spain) in the near future. BERRILUR aims for the promotion of the development and acquisition of the knowledge needed to place the Basque Country within the “European Map of Excellence” on polluted soils and sediments.

Through this project, we will help achieve the objectives and guidelines established in the Basque Environmental Strategy on Sustainable Development (2002-2020) regarding environmental R&D. Finally, BERRILUR, a strategic action submitted by GAIKER and LABEIN, with the participation of five Departments of the Basque Country University, the Basque Institute of Agricultural Research and Development (NEIKER), and EUVE perfectly fits into the priorities described in the PCTI 2001-2004.

2. Soil contamination problems in the Basque Country

In the context of the efforts to provide good quality of the life for the public one of the priorities of the environmental sustainability strategy must be to ensure clean , healthy water air and soil.

The deterioration of the soil due to contamination is a serious problem in whole Europe particularly in small and very densely populated countries , like the Basque Country. No further increase is expected in the extent of the land contaminated, as a commitment is in place to prevent this, but the large number of areas (close to 7,000 potentially contaminated sites have been detected which an occupancy of around 7500 hectares) already contaminated pose a huge challenge for the coming decades.

Urbanised areas account for around 4 % of the total surface in BAC (Basque Autonomous Community). Demand for housing, transport infrastructures and large commercial and recreational facilities is expected to increase in the coming years. The total area occupied for industrial ruins is over 3 million m². Recovery of these sites is an alternative to the growing occupation of virgin land

3. BERRILUR RTD initiatives

Five different RTD initiatives have been designed within the BERRILUR initiative. Activities on these

¹ Other Participants In Berrilur Project:

Fundacion Labein, Fundacion Euve, Fundacion Neiker, Basque Country University –Euskal Herriko Unibertsitatea

RTD projects have began January 2004 and they will finish in three years:

Basque participants in RTD activities are:

MEMBER NAME	ROLE IN BERRILUR
FUNDACION GAIKER	Co-ordination of BERRLUR and leader of the activities 1 and 4
FUNDACION LABEIN	Leader of the activities 2 and 5
EUVE	Participant
NEIKER	Participant
UPV-EHU: DPTO.QUIMICA ANALITICA (FACULTAD DE CIENCIAS)	Leader of the activity 3
UPV-EHU: DPTO.QUIMICA ANALITICA (FACULTAD DE FARMACIA)	Participant
UPV-EHU: DPTO. DE BIOLOGIA VEGETAL Y ECOLOGIA	Participant
UPV-EHU: DPTO. DE INGENIERIA QUIMICA Y DEL MEDIOAMBIENTE (ESCUELA DE INGENIEROS)	Participant
UPV-EHU: DPTO ZOOLOGÍA Y DINÁMICA CELULAR ANIMAL	Participant

Activity 1

Research on contaminant availability in polluted soils of the Basque Country.

Activity 2

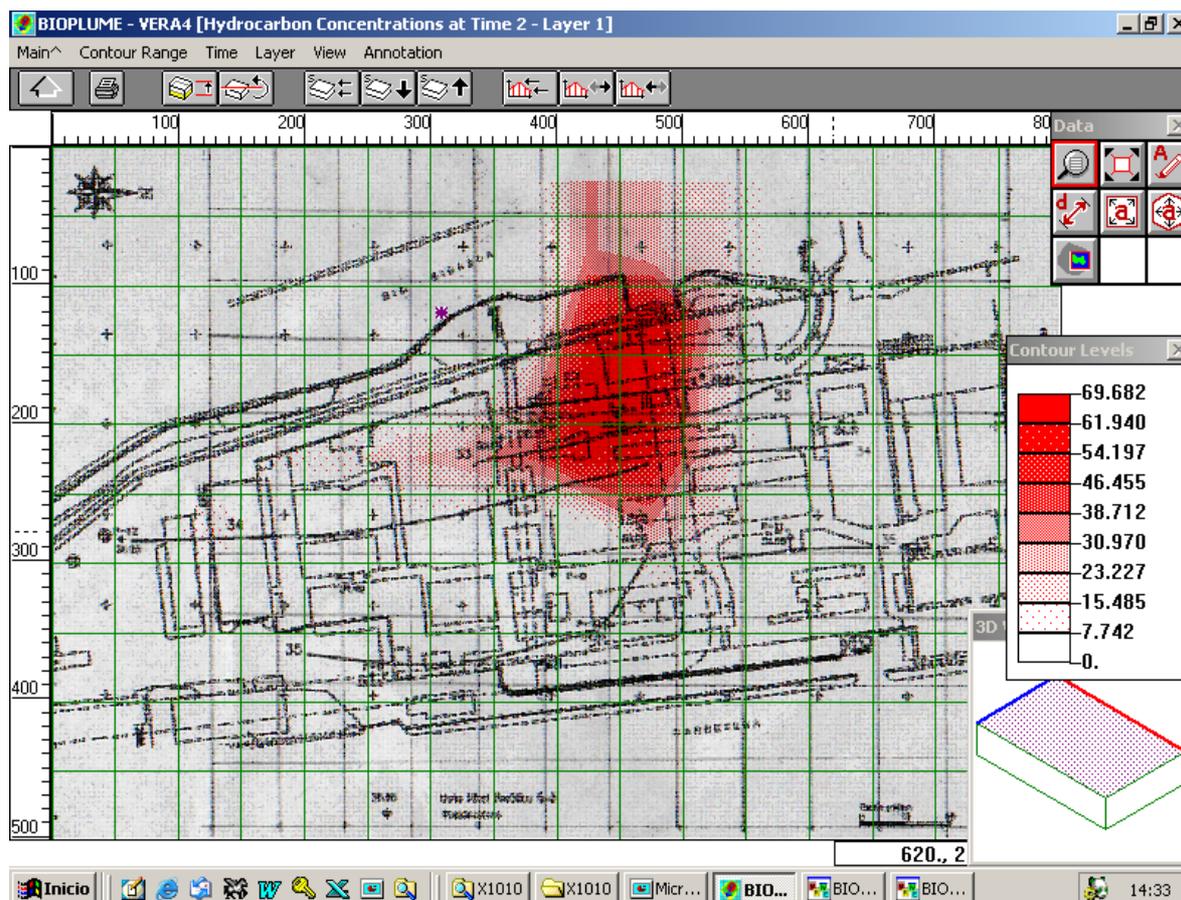
Development of protocols, procedures and indicators for the selection of the most appropriate strategy to be used when approaching the remediation of polluted soils, sediments, and groundwater.

Activity 3

Research on the remediation of soils polluted with organic compounds through the utilization of low temperature techniques.

Activity 4

Assessment of natural attenuation as a valid technology to recover degraded sites within the Basque Country.



Activity 5

Remediation of soils and sediments polluted with a mixture of organic and inorganic (*i.e.*, heavy metals) contaminants using plants (*i.e.*, their capacity to extract and/or degrade contaminants).



4. Acknowledgements

This work has been financially supported by the ETORTEK programme from the Basque Government, through the BERRILUR project, ref. IE03-110. IHOBE S.A support for this project is kindly acknowledged

Assessing the impact of tile drainage on flow generation and nutrient export on catchment scale

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1. Introduction

Tile drainage, which is common agricultural practice to improve moisture and aeration conditions, shortens the residence time of water in the biologically active unsaturated zone and therefore enhances diffuse pollution of adjacent surface water bodies with nutrients or pesticides (Southwick et al., 1995; Tomer et al., 2003). Often, tile drainage is accompanied by flow anomalies causing further, unexpected acceleration of water flux and solute transport towards the tile drains (Lennartz et al., 1999; Kohler et al., 2003). Given that the catchment boundaries can be defined and a virtually impermeable layer underlies the tile drains, tile drained fields can be considered as big lysimeters and are therefore ideal for studies on solute transport at the field scale (Lennartz et al., 1999; Richards & Steenhuis, 1988). However, to evaluate the environmental impacts on surface water bodies, it is a matter of particular interest how the drainage discharge and its solute signal translates to the next scales. Therefore, we present a general concept to investigate the combination of tile drainage and preferential flow on different scales.

2. Material and Methods

In November 2003, a hierarchical measurement program was initiated in the small, predominantly rural catchment (16 km²) of the brook Zarnow near Rostock in north-eastern Germany. Sampling stations for discharge measurement and water sampling are located at the drain outlet of a tile drained field site (4.2 ha) and at an adjacent ditch draining around 180 ha used for crop production by conventional farming. The drainage depth is 1.1 m and the drainage spacing of the fan-shaped drainage network varies between 8 and 22 m. Further sampling stations are situated at a ditch, which drains about 50 ha grassland used as meadow and pastures by small ditches and occasional tile drains, as well as at the brook Zarnow, which is met by both ditches. At the tile drain outlet, the water level in a Venturi flume was recorded in 15 minute intervals, while an automatic sampler (ISCO) took samples every two hours, which were then merged to daily composite samples. At the three other sampling stations, manual sampling and discharge gauging was carried out daily to twice a week depending on meteorological conditions. All samples are analyzed for nitrate and other relevant ions (SO₄²⁻, Cl⁻, Ca²⁺, K⁺, Mg²⁺ and Na⁺) using ion chromatography. Further investigations include a soil survey, the operation of a weather station, the monitoring of the groundwater level and manual as well as GPS surveying of the ground surface and the ditch network. The use of a real-time kinematic GPS system with a local reference station and a car-mounted rover station moving along machine tracks allows the acquisition of ground elevation data of good quality within reasonable time.

3. Results and Discussion

The combination of a digital elevation model (2.5 m grid) generated with the interpolation method Kriging (errors estimated by cross validation: RMSE 2.6 cm, maximum error 15 cm) with a map of the tile drainage network is shown in Fig. 1. The second sampling station is no longer operated, but two years of daily data are available for both stations. Although different data sources are used, the flow direction of the tile drains and the location of the watershed between tile drained units agree quite well. Therefore, these data can be used in further work to explicitly account for drainage structures and for the topographical characteristics of the drainage units which not only defines the surface processes but also the slope of tile drains.

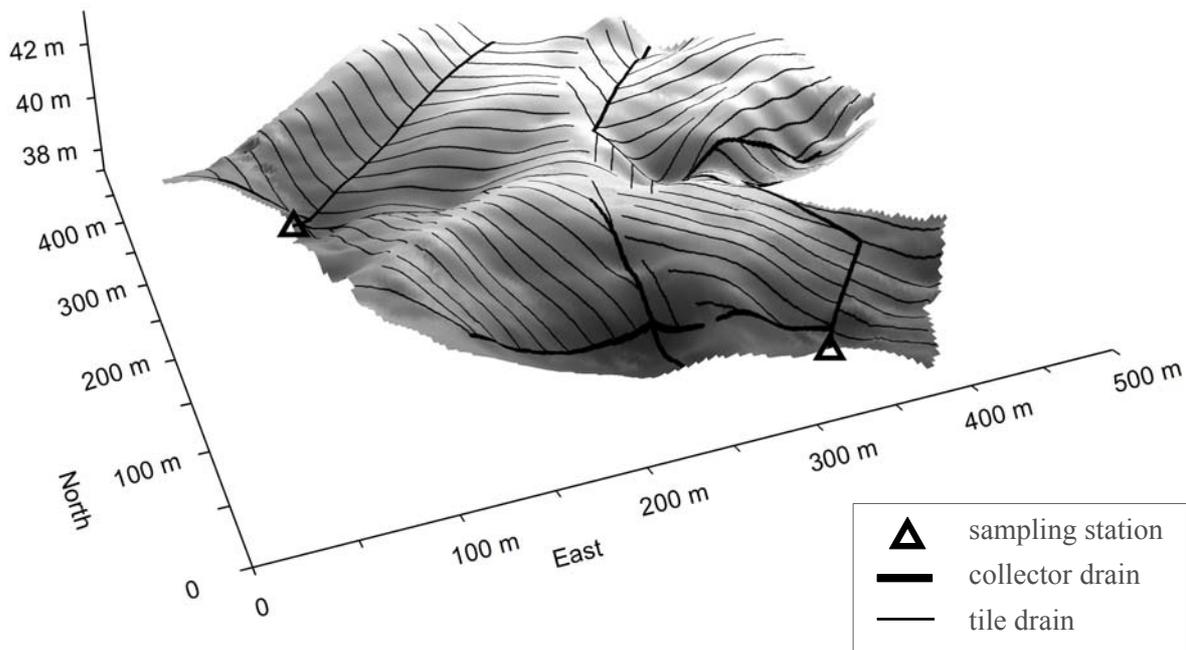


Figure 1: Digital elevation model for the tile drained field sites (approx. 10 ha)

First daily data of the four sampling stations is shown in Fig. 2. After the very dry summer of 2003, until the middle of January 2004, nearly all precipitation replenishes the soil storage without causing major changes in discharge. The onset of drain discharge coincides with the occurrence of higher flows not only in the ditches, but also in the brook. Additionally, the close temporal agreement – at least on the basis of daily data – between drainage discharge and brook discharge also indicates that tile drainage plays a very important role for flow generation on the scale of the brook. After the onset of drainage flow, the response of the associated ditch and the Zarnow to precipitation is nearly as fast as that of the tile drains, which shows an average lag time of 5 hours, while the maximum flow of the grassland ditch does not occur until the following day. Though the response of the drains to rainfall was fast, the recession of the tile drain discharge was comparable to that of the brook pointing to a strong matrix flow component during this phase. Hydrological modelling will therefore hypothesise that tile drain discharge is composed of two components with a fast tile drain discharge representing preferential flow and a component originating from matrix flow. This separation of the tile drain hydrograph is also applied in tracer studies (Kohler et al., 2003). In ditches and in the brook, a baseflow component will also be present.

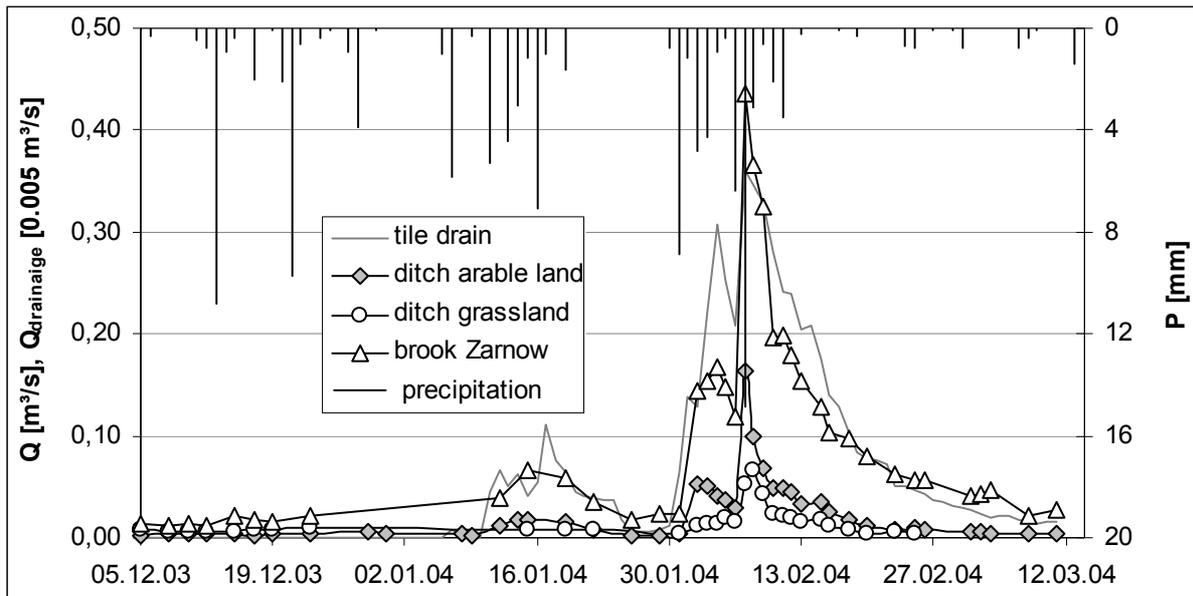


Figure 2: Daily precipitation and daily discharge at different scales

Regarding the monitored solute concentrations, we focus on the nitrate concentration during the main discharge event (31.01. - 23.02.04). Generally, high drain discharge rates correspond to high nitrate concentrations: between the *daily* tile drain discharge and the nitrate concentration, a nearly linear relationship ($R^2 = 0.75$) could be observed. In contrast, dilution effects are rare and could only be detected to some extent during the first peak (31.01/01.02.04) of the event (Fig. 3). Fast flow components therefore tend to displace soil water with high nitrate concentration. The concentration of the geogenic sulphate shows opposite behaviour compared with the nitrate of mainly anthropogenic origin, especially during the first and the third peak of the event. During the recession of the hydrograph, matrix flow determines the solute concentrations, as the sulphate concentration rises again, while the nitrate concentration stays on a relatively high level indicating ongoing supply from the nutrient enriched soil.

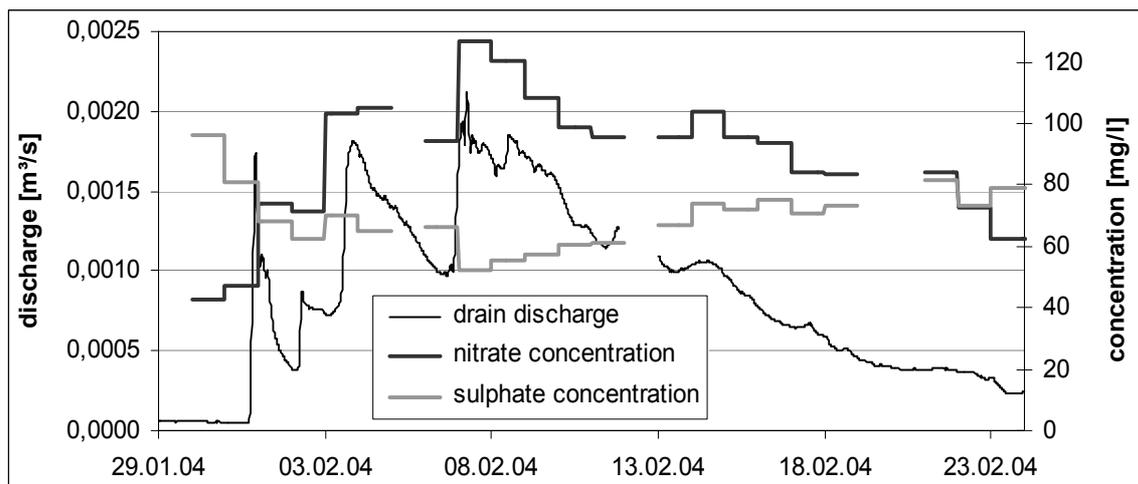


Figure 3: Drain discharge in 15 minute intervals, nitrate and sulphate concentrations from daily composite samples. Missing data caused by failure of the sampler pump or of the pressure transducer due to frost.

Figure 4 displays the nitrate concentrations of the tile train outlet, the two ditches and the brook during the main discharge event. The solute concentrations at all scales show a concurrent behaviour pointing to the importance of drain discharge solute concentrations for the overall water quality. Also at the scale of the ditches and the brook, nitrate concentrations are discharge dependent with high concentrations – and therefore high loads – coinciding with high flows (compare Fig. 2) as found in comparable studies (Tomer et al., 2003), though the relationship is rather logarithmic than linear. The latter, and the lower concentrations in the ditch draining arable land and the Zarnow compared to the tile drain discharge indicates the contribution of less polluted groundwater component to the total flow. Nitrate concentrations, especially those of the grassland ditch, stayed on a high level at the end of the event and also at the end of the discharge period indicating that a high amount of nitrate is still available in the soil. Though the hydrological response of the grassland ditch was delayed, solute concentrations varied strongly compared to the other stations. In November 2003, nitrate concentrations were $< 1 \text{ mg l}^{-1}$, while the highest nitrate concentrations of all stations were also measured in the grassland ditch, which drains a catchment largely covered by shallow peat soils. The drainage and the resultant aeration of peat enhances the decomposition of organic matter and therefore leads to high concentrations of nitrate and other solutes (Martin et al., 1997) in the pore water, particularly if dry and wet periods alternate. This process probably explains why the nitrate concentrations of the grassland ditch exceed even those of the tile drain discharge from heavily fertilized arable land.

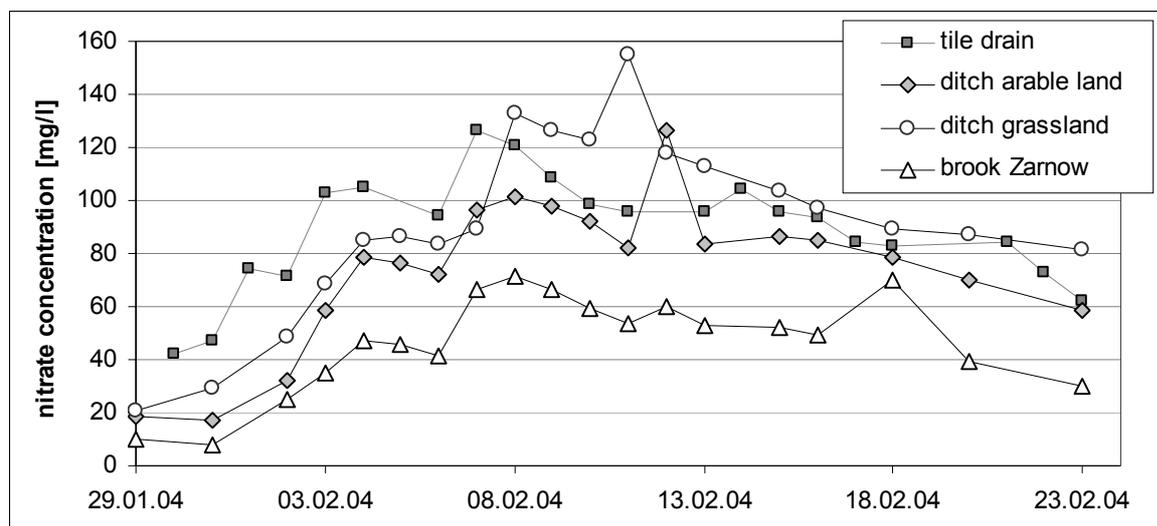


Figure 4: Nitrate concentrations of the tile drain, the ditches, and the brook show a similar

4. Conclusions and future work

The data acquired during the first discharge period of the presented project show that tile drainage discharge is composed of a fast and a slow component, while in ditches an additional baseflow component is present. Tile drainage and brook discharge behaved in a similar fashion indicating the importance of tile drains for the hydrological response and the water balance of the Zarnow catchment. At all scales, high nitrate concentrations coincided with high discharges. Nitrate concentrations are still elevated at the end of the discharge period indicating heavy nutrient enrichment of the soil, and solute exports from the grassland site may not be neglected due to very high concentrations.

The fast response of the tile drains shows clearly that daily data alone is not sufficient for the detailed investigation of fast flow components even in a lowland catchment. Mechanisms triggering the fast flow have to be investigated. Therefore, the temporal resolution of the ongoing monitoring is increased by installing ISCO-samplers and pressure transducers at the ditches and the brook. The aim of future modelling is to depict how the drainage components as well as solutes translate to the next scales. Therefore, tile drainage will be incorporated into the distributed model MHYDAS (Moussa et al.,

2002), which accounts for man-made structures and contains a fast flow component.

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Monitoring of multi-analyte mixtures in water by an optical sensor system: a new approach for reducing the required sensor number

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Abstract: Within this contribution, we focus on the Reflectometric Interference Spectroscopy (RIFS) as an optical sensor system for the quantification of multi-analyte mixtures in water. The main benefit of this work is based on time-resolved measurements of the interaction between sensitive polymer films and hydrocarbons in water. The application of artificial neural networks for the evaluation of such time-resolved measurements including additional temporal information allows reducing the required sensor number and therefore a simplification of the complete sensor set-up.

1. Introduction

The efficient protection of soil and water requires powerful analytical tools for the assessment of contaminated matrices on the one hand, and for the control of decontamination procedures on the other hand, whereby in most cases the quantification of multi-analyte mixtures is of great interest. For this purpose, most of the common analytical methods require a time and money consuming sampling on site followed by the transport to a laboratory. In contrast to this, a sensor system enables a real-time quantification on-line or even in-line the environment of interest. As a sensory approach is not based on a separation effect like GC or HPLC the quantification of a multi-analyte mixture requires a sensor array in which different sensitive polymer films are combined. For the calibration of such a sensor array normally different characteristics of the obtained sensor signal like the area, the slope at a certain point of time or the height at the equilibrium as shown in Fig. 1 (left hand site) are used.

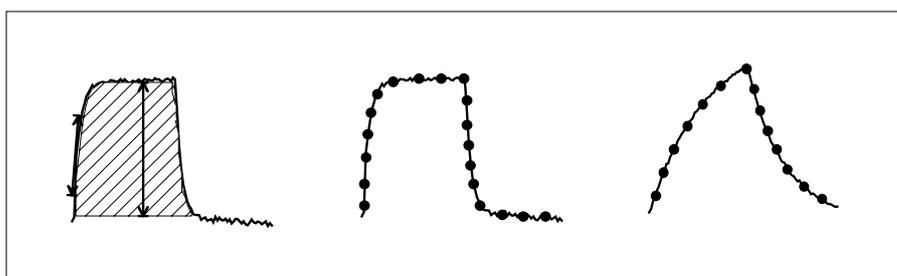


Figure 1: Possibilities of sensor signal evaluation

The main lack of this approach is that the common multivariate calibration methods for the quantification of multiple analytes in mixture need as many sensor signals respectively sensors in the array as analytes to be quantified otherwise the system would be statistically underdetermined.

In contrast to such static sensor measurements, Dieterle et al have established a new approach in our group for reducing the number of required sensors [1]. This approach is based on the exploitation of the time-specific information of sensor responses. If the various analytes of a mixture show different kinetics for the sorption into the different sensitive polymer layers caused for example by a different size or polarity of the analytes, the resulting sensor response recorded versus time features a different shape for these analytes as shown on the right hand site in Fig. 1 for a swift and a slow interaction

kinetic. This additional temporal information of such time-resolved sensor measurements can render the parallel information of different sensors in an array redundant allowing reducing the number of sensors.

The feature and widespread opportunities of this approach are demonstrated within this work on hand by considering as example the quantification of a quaternary mixture of the low alcohols in water from methanol to 1-butanol. In this homologous series, the analytes differ from each other only by additional CH₂ groups. The differences of the analyte size (0.068 nm³ to 0.180 nm³) allow a systematic investigation of the quantification based on different kinetics of sorption into the polymer layers.

2. Material and methods

2.1 Measuring Principle – Reflectometric Interference Spectroscopy

The Reflectometric Interference Spectroscopy (RIfS) is based on the multiple reflectance of a white light beam at a layer system as shown in Fig. 2 consisting of a glass substrate, a sensitive polymer film and the surrounding for example water. The parts of the beam reflected at different interfaces of the layer system superimpose, so the intensity of the reflected light dependent on wavelength shows an interference pattern. If an interaction between the sensitive polymer layer and analyte molecules in the surrounding takes place, a reversible swelling effect of the polymer film correlated with changes in optical thickness, which is given as the product of physical thickness and refractive index, can be observed. This leads to a shift of the interference pattern, which can be monitored by fitting a mathematical function to a local extremum. Therefore, finally, the sensor signal is given as changes in optical thickness depending on time during analyte exposure.

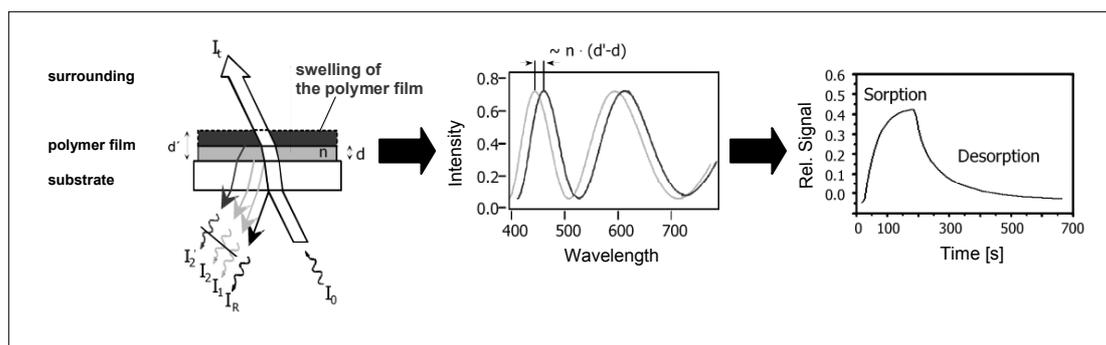


Figure 2: Measuring principle of RIfS

2.2. Polymer materials

In order to realise the presented approach, obviously it is quite important to have polymer materials at our disposal, which show different interaction kinetics with different analytes of interest. In this case, three different polymer systems have been used as sensitive layers. Fig. 3 shows the chemical structure of these polymer systems, on the one hand a commercial polyimide system (a), which features a micro porous structure with a mean pore size of 0.118 nm³, and on the other hand two hyperbranched polyester (HBP) systems with two different functional groups in the linear side chains (b). The Institute of Polymer Research Dresden kindly placed these hyperbranched polyesters at our disposal.

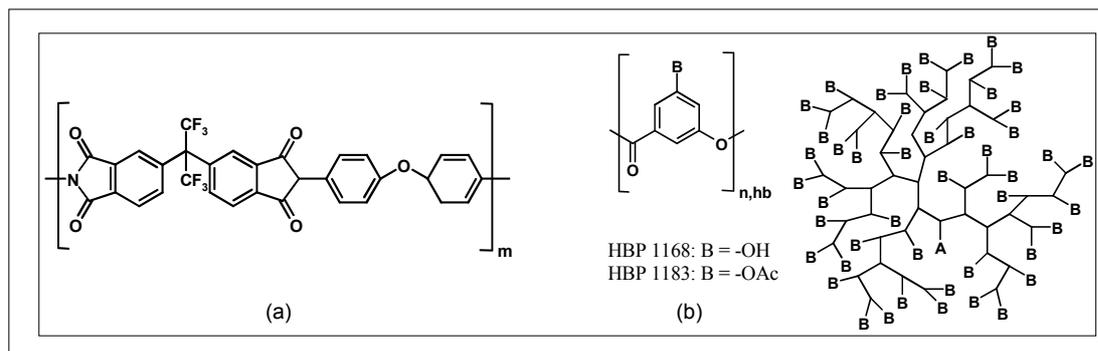


Figure 3: Polyimide PI 2566 (a) and hyperbranched polyesters with different functional groups (b)

2.3 Data sets

In addition to single analyte measurements, two multicomponent data sets were recorded for the multicomponent analysis of quaternary mixtures. Based on a full factorial experimental design a calibration data set consisting of 256 mixtures of the four homologues alcohols and a validation data set consisting of 81 quaternary mixtures were measured. It is noteworthy that all concentration levels of the two data sets differ at the highest possible distance. Thus, the validation data set should give a realistic estimate of the network performance in a real world situation. The sensitive layers were exposed to the mixtures for 22 minutes and afterwards to pure water during 22 minutes for recovery. During the sorption and desorption process, the signal of each sensor was recorded with a resolution of 78 data points resulting in a total number of 234 data points for all three sensors. These data points were used as independent variables for a multivariate calibration.

2.4 Data evaluation

As mentioned before, the evaluation of time-resolved measurements requires artificial neural networks, in particular in order to acquire non-linear effects of the interaction between sensitive polymer layers and analytes. The neural networks implemented for this study belong to the class of the multilayer feedforward backpropagation networks, which are in detail described by Patterson [2].

The main step during the data evaluation is represented in the extraction of the temporal information of the sensor signals needed for the quantification of the multi-analyte mixture and the separation of these information from redundant data points. This was carried out by variable selection, which is based on growing neural networks. Afterwards, the final prediction of the analyte concentration in the mixture was done by using an optimised network, which was built up based on only these specific data points including the significant temporal information.

3. Results and Discussions

3.1 Characterisation of the interaction kinetics of the single analytes

As pointed out in the introduction, a fundamental pre-condition for the successful application of this new approach is a difference in interaction kinetics. Fig. 4 shows the changes of optical thickness of the three polymer films during analyte exposure. It can be seen that methanol shows a rather swift interaction with all three different polymer systems by reaching the equilibrium state within a few seconds. As suspected, the sorption of the bigger sized ethanol into the micro porous polyimide structure is inhibited, leading to a slower interaction kinetic. By comparing the swelling behaviour of the polyimide during interaction with the next homologues alcohols 1-propanol and 1-butanol, it is obviously that a bigger sized molecule shows a rather slow interaction kinetic. In contrast to this, the two hyperbranched polymer systems show a rather different behaviour, so only for 1-propanol and 1-butanol a difference in interaction kinetics is observed. This distinction might be caused by a difference in polarity and by a difference in branching degree of the two systems.

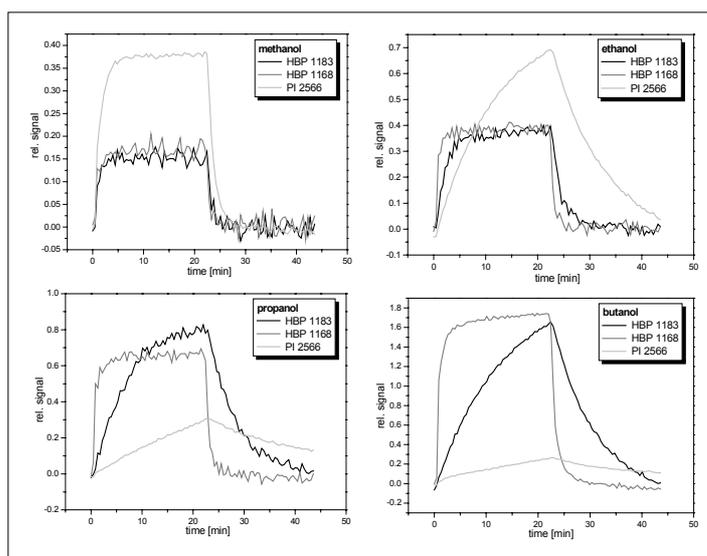


Figure 4: Swelling behaviour of the different polymer systems

In summary, a combination of these polymer systems results in a sensor array, in which each sensor show a different interaction kinetic with the four homologous alcohols.

3.2 Quantification of a quaternary mixture by the use of artificial neural networks

Based on the different interaction kinetics and the different temporal information of the resulted sensor signals, a quantification of a quaternary mixture by the use of artificial neural networks should have been performed. In a first step, the significant temporal information was extracted by the use of a growing neural network algorithm as presented in chapter 2.4. As a final result of this variable selection figure 5 shows the information content of different data points, whereby only such data points are considered, which have been used for the final prediction of the validation data by the optimised neural network. Obviously, the information content of the single data points is rather different, so it is noteworthy, that only 15 of the primal 234 data points carry the information needed for the quantification of the quaternary mixtures of the validation data set.

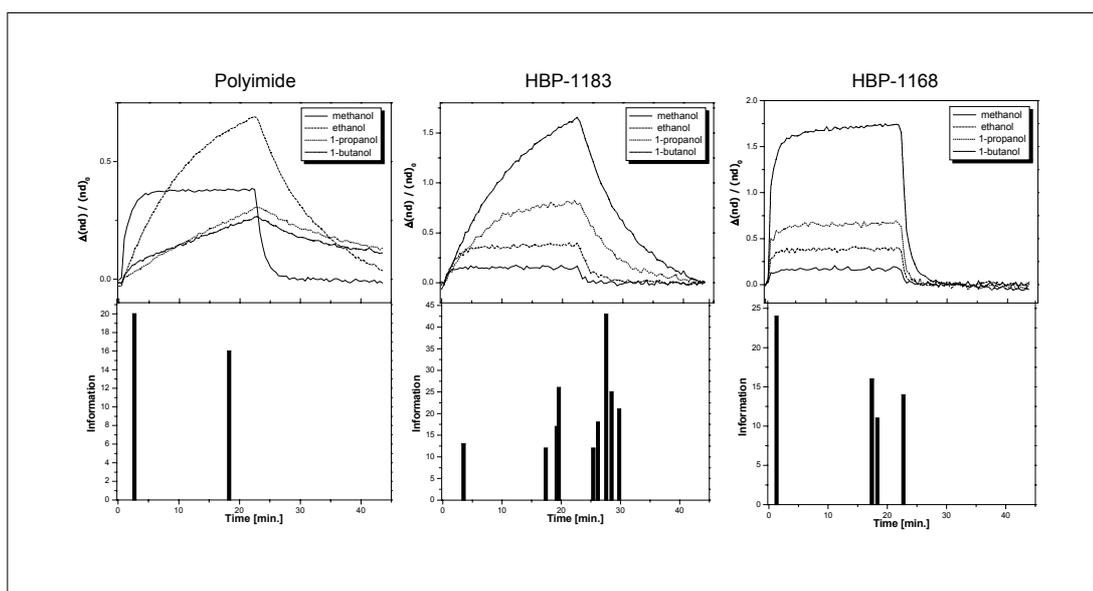


Figure 5: Different temporal information of the different sensor signals

In Tab. 1, the relative root mean square errors RMSE for the prediction of the validation data by using either a different number of data points (a), (b) or different sensors (c)-(d) are listed. The success of the variable selection becomes clear by the fact, that the predictions of the validation data by the network, which uses only 15 variables and which was trained by the calibration data set (b), are by far better than the predictions of the network using all variables (a). The mean of the relative RMSE for all four analytes is nearly halved.

Table 1: Relative root mean square errors for the predictions of the validation data

Method	Methanol	Ethanol	1-Propanol	1-Butanol	Mean value
(a) All variables	24.3%	28.3%	34.3%	24.8%	27.9%
(b) 15 variables	14.4%	17.1%	30.8%	20.3%	20.6%
(c) HBP 1168	53.2%	52.9%	49.3%	29.5%	46.2%
(d) HBP 1183	32.3%	28.8%	31.1%	21.9%	28.5%
(e) PI 2566	15.9%	21.9%	44.7%	37.2%	29.9%
(f) HBP 1183 / PI 2566	14.1%	19.1%	30.0%	22.8%	21.5%
(g) 3 static sensors	55.7%	27.9%	47.6%	236%	38.7%

An interesting point is the simulation of single-sensor setups by using only the data points of one sensor for the data analysis. If the time-resolved shapes of the sensor signals of a sensor as shown in figure 4 before differ enough, a single-sensor setup should be feasible. Therefore, neural networks using only the variables of one sensor were trained by the calibration data set and subsequently predicted the validation data. The prediction errors using different single sensors are also listed in table 1 (c)-(e). It is obviously that methanol and ethanol are best predicted using the polyimide sensor whereas 1-propanol and 1-butanol are best predicted using the HBP 1183 sensor. So finally, the combination of time-resolved measurements of the HBP 1183 sensor and of the polyimide sensor should be enough for the quantification of all 4 alcohols in a quaternary mixture (f).

In the end we want to focus on the comparison of the time-resolved approaches with common static sensor measurements, which use only one single feature per sensor response. Thus, the heights of the signals of all three sensors just before the end of exposure to analyte were used for the calibration of neural networks. As the quantification of 4 analytes by 3 variables with no constraints of the concentrations is mathematically underdetermined, as expected, the results are very poor (g).

4. Conclusions

The fundamental investigations presented here clearly demonstrate the possibilities of the combination of an optical sensor system with modern chemometric tools like artificial neural networks. The quantification of a multi-analyte mixture of environmentally relevant components in water with a minimum of required sensors enables the simplification of the complete sensor set up. So, finally, this approach as shown in principle here can be considered as an important step on the way to a modern and powerful analytical tool as required for many applications in environmental protection.

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Soil pollution by heavy metals in the region of the reserve Baltata (Black Sea)

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1. Introduction

The Batova River Catchment Basin creates conditions for a high biodiversity existence close to the Black Sea. A part of this natural landscape was separated as a supported reserve “Baltata” declared in 1962 with the aim to protect a typical dense forest. Rich pay dirt Mn – ore deposit was discovered in 1960s in the close proximity of the Batova River. In present, the Mn-ore deposit is allotted as a claim to two companies. One of the ore-mine, which is being operated by the Bulgarian – Swiss company “Euromangan” Ltd., functioned for a long time. Its non-reclaimed slime – pit near the village Odartsi, contaminates the land with dust, which contains Mn-Fe compounds.

The purpose of the present research is the determination of the soil and plant contamination.

The subject of the research is the region of the Batova River Catchment Basin, in which the Reserve Baltata, the Resort Albena and the slime-pit are situated.

The Batova River Catchment Basin covers 38 053 ha, in which 47% are agricultural land, 31% - are forest land and 22% are settlements, roads, resorts and etc.

This report is a part of the project called “Ecological Estimation and Forecast for the Environment of the Batova River Catchment Basin”, financed by the Resort “Albena”Ltd.

2. Material and methods

56 soil and vegetable simples are taken and analysed from 33 representative simple plots, situated in different distances from the main resource of pollution.

The main zonal soil type is the Chernosems (FAO). However, the Orthic Luvisols (FAO) is a widespread soil type as well.

The azonal soil types are:

- Ranker - on separated spots in some landslides
- Fluvisols (FAO)- on the downstream of the Batova River.

All soil sample plots are morphologically described.

The soil samples are analysed by the following methods:

- mechanic composition – Kachinski
- pH – pH meter
- humus - Tjurin
- Heavy metals, Ar, S and alkaline metals – ICP

3. Results and Discussion

The results of the present investigation are presented in table 1 (Concentrations of some heavy metals, S, As in the soils of the Batova River Catchment Basin) and table 2 (*Concentration of some elements in the leaves samples from the region of the Batova River Catchment basin*)

According to Cheshire et al. (1997) Mn is combined with the fulvoacid in the upper soil layer. Microbiological activity plays an important role in the soil process of oxidation and in the formation of the Mn concretions (Aristovskaia).

Stoyanov (1999) marks that the dissolved Mn forms predominate in the acid soils which are rich in organic material.

- The waste products from the Mn- ore dressing, stored in the slime – pit “Odarsti” and in the non-organised waste piles contain Mn ten times above the average (Stoyanov, 1999) and 54-84 times above the natural background value for Bulgarian soils (800 mg/kg). The Mn concentrations in the soils are significant under the average and natural background concentrations. These data shows that Mn is significantly accumulated from the waste pile.
- An augmentation of Mn value in the debris and grass layer exists.
- All analysed soils and waste materials contain Fe and Fe₂O₃ above the value, which determine them as rich and highly rich.
- Pb- concentrations in the soils samples are in values over the natural background for the country
- Ni- concentrations are also over the natural background in the waste materials from the slime – pit “Odarsti” and in the soils which are close to that slime – pit - on the land of the villages Tsarkva, Prilep and Batovo.
- The buffer capacity of the soils from the region is high which provide a low mobility of the heavy metals and theirs assimilations by the vegetation.

The Mn contents in the plants, according to Stoyanov (1999) depend on its soil value and soil acidity. The plants do not assimilate Mn from the soils with a low hydrogen ion concentration. Heenan et al. (1980) mentioned that there is a transfer from old to young leaves in case of deficit. High Mn concentrations in the soils decrease the microelements assimilation by the plants.

From data shown in table 2, it can be concurred that the Mn concentrations varies in a large degree. Its concentration in some leave simples as from P5 is twice higher than its declared toxic by Pendias (Kabata – Pendias et al., 1989). The variety of the Mn concentrations in the leaves samples may be explicated by the different quantity of dust with high Mn concentrations, which is sedimented over the plants.

Table 1: Concentrations of some heavy metals, S, As in the soils of the Batova River Catchment Basin

№ simple	depth	pH /H ₂ O/	Mn %	Fe %	Pb mg/kg	Zn mg/kg	Cu mg/kg	Ni mg/kg	Co mg/kg	Cd mg/kg	Cr mg/kg	As mg/kg	S %
P ₁	Slime-pit "Odartsi"	8,3	875	1,950	40,0	75,4	125,1	162,8	44,7	0,4	3,0	<	0,192
P ₇	Village Tsarkva 0-12	7,63	0,470	2,423	51,5	75,1	111,1	54,8	17,6	2,8	17,8	<	0,163
	12-30	8,29	0,160	2,316	35,5	67,1	89,7	46,1	14,1	1,2	19,3	<	0,178
P ₈	Village Tsarkva 0-10	7,16	0,095	2,051	29,1	55,8	67,9	41,2	12,1	0,9	19,7	<	0,026
	10-30	7,41	0,105	2,185	31,7	54,7	53,3	36,4	12,7	1,2	15,2	<	0,071
P ₁₀	Village Batovo	7,93	0,021	1,178	17,3	40,5	33,6	23,0	6,8	0,3	26,6	<	0,105
P ₁₂	Field, village Prilep	7,34	0,046	1,910	26,1	55,0	47,5	48,5	7,7	0,7	20,6	<	0,091
	Village Prilep	6,62	0,038	1,903	25,3	69,9	49,2	53,7	10,6	0,8	59,9	<	0,098
P ₁₄	0-5	6,94	0,077	2,032	28,3	73,2	62,3	33,9	11,4	0,9	16,6	<	0,082
	5-20	7,28	0,043	2,192	28,3	70,5	55,9	39,5	12,1	1,0	25,3	<	0,095
P ₁₇	Meadow road village Batovo - village Tsarkva	6,71	0,030	1,686	32,1	52,9	66,1	30,4	9,5	<	19,5	<	0,103
	12-25	7,57	0,038	2,142	28,3	51,8	54,4	34,1	11,1	0,7	17,6	<	0,171
P ₃₁	Reserve Baltata debris layer	7,48	0,088	1,824	29,1	63,0	42,4	28,7	8,9	1,1	12,1	<	0,156
	Reserve Baltata 0-18	7,69	0,031	2,136	29,9	61,9	43,3	32,1	10,5	1,9	13,3	<	0,128
P ₃₁	18-30	8,02	0,023	1,390	15,2	36,9	32,2	18,7	7,1	<	12,5	<	0,100
	Reserve Baltata A ^I (g) 0-16(16)	7,12	0,036	2,715	36,3	73,4	85,4	37,9	11,0	1,1	43,0	<	0,160
P ₃₂	A ^{II} (mm) 16-40(24)	6,71	0,027	0,028	13,4	21,4	63,0	5,0	1,4	0,3	12,1	<	0,415
	0-16(16)	7,20	0,033	2,151	38,4	73,8	126,3	28,6	9,7	1,3	32,8	<	0,115
P ₃₃	Natural background value (according to Regulation, №3, /OJ Nr..39/2002)	>6	**0,5	**5,5	26	88	34	46		0,4	65	10	0,085*

* Average concentrations according to Vinogradov, A., 1962

** Average concentrations according to Stoyanov, S., 1999

Table 2: Concentration of some elements in the leaves samples from the region of the Batova River Catchment basin

N Sample plot	Mn	Fe	Ca	K
	mg/kg		%	
P ₅	935,0	193	7,847	2,216
P ₆	356,1	127	6,983	1,598
P ₇	1146,0	766	4,088	1,643
P ₈	108,4	79	9,658	1,114
P ₉	114, 0	351	9,880	3,330
P ₁₀	49,0	143	8,490	2,003
P ₁₂	25,0	82	10,460	1,646
P ₁₄	30,9	135	6,405	1,758
P ₁₇	75,5	115	6,139	1,285
P ₃₃	27,5	290	8,438	2,003
P ₃₃ Syringa vulgaris	264,6	6039	7,962	0,478

4. Conclusions

Anthropogenic activities, especially the experience of the ore- mine company which is situated near to the Reserve Baltata will drastically change the dense forest ecosystems by:

- drying the territory;
- depositing the active Mn dust upon the vegetation and soils.

According to our results soil and vegetation monitoring programmes are requested. The observed territory must be established by the modeling of the emission spreading from the studied sources of contamination. The monitoring will be useful for the understanding of the soil processes.

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