In situ bioremediation of groundwater contaminated by herbicides from point sources

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Environment & Resources DTU
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Preface

This thesis is based on the research done for a PhD project undertaken from 1999 to 2002 at Environment & Resources DTU, Technical University of Denmark. The primary supervisor was Professor Poul L. Bjerg and the co-supervisor was Associate professor Hans-Jørgen Albrechtsen, Environment & Resources DTU. The project was funded by the Technical University of Denmark and a travel grant was given by “Amternes Videnscenter for Jordforurening”.

The thesis is composed of a summary of the subject “In situ bioremediation of groundwater contaminated by herbicides from point sources” as well as 6 journal papers (3 published, one accepted for publication and two manuscripts) and a conference paper (in press). However, the papers are not included in this www-version but can be obtained from the Library at Environment & Ressources DTU, Bygningstorvet, Building 115, Technical University of Denmark, DK-2800 Lyngby (library@er.dtu.dk).

The in-text references and the titles of the papers are:


As part of my PhD project I have conducted field and laboratory experiments, participated in four international conferences, visited four universities in North-America, been a member of an expert group on two projects for “Amaternes Videnscenter for Jordforurening”, participated in several Danish meetings and contributed to Danish journals.

I would like to thank a number of people who have helped me along the way. Great thanks to my supervisors Poul L. Bjerg and Hans-Jørgen Albrechtsen, for their never-ending interest and support. Thanks also to my co-authors with whom it has been stimulating and a pleasure to collaborate.

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All my colleagues at Environment & Resources DTU are gratefully acknowledged for their help and pleasant company these last years. A special thanks to Philip G. Pedersen, Lars Toräng and Anders Baun who have commented on my manuscripts.

The hospitality I was met with by Peter Adriaens, University of Michigan, Roy Spalding and Pat Shea, University of Nebraska, Bill Hickey, University of Madison-Wisconsin, and Jim Barker, University of Waterloo is greatly appreciated.

And finally, thanks to my friends and family who have been very patient with me – especially during the last months of this PhD project.

Nina Tuxen
Abstract

This thesis consists of a summary of the subject “In situ bioremediation of groundwater contaminated by herbicides from point sources” as well as 7 papers describing the experimental work undertaken for the PhD project.

A significant part of the pesticides found in groundwater probably originate from point sources such as old landfills, machine pools, market gardens and accidental spills. Point sources are characterized by relatively high pesticide concentrations in a limited amount of water. This characteristic makes assessment of remedial actions towards pesticides in groundwater from point sources relevant.

Eight of the most frequently used and found pesticides were chosen for this study. They were: MCPP (mecoprop), dichlorprop, 2,4-D, DNOC, isoproturon, atrazine, BAM (a metabolite of chlortiamid and dichlobenil), and bentazone. These are all herbicides though with various characteristics.

Sorption of the 8 selected herbicides was found to be limited in the present investigation, in agreement with previous research conducted in sandy aquifers. Retardation factors ranged from 1 to 3 for the phenoxy acids (MCPP, dichlorprop, and 2,4-D), BAM, and bentazone. Sorption of isoproturon, atrazine, and DNOC was slightly higher in aquifers with relatively high organic carbon content or low pH, resulting in retardation factors up to 10. Only the neutral fraction of the weak acid DNOC was sorbed and consequently, the retardation factor was strongly dependent on pH.

A literature search regarding degradation of the herbicides was conducted to supplement the degradation experiments which were performed. All 8 herbicides were found to be recalcitrant under certain aquifer conditions. However, with few exceptions, the phenoxy acids were readily degradable under aerobic conditions. Also DNOC, isoproturon, and atrazine could be degraded in some aquifers. No investigations reported degradation of BAM or bentazone in aquifers. Thus the potential for bioremediation of herbicides seems most promising for the phenoxy acids.

A field injection experiment was conducted in a shallow, aerobic aquifer. The two injected phenoxy acids, MCPP and dichlorprop (40 µg/L each), were quickly degraded after a lag period of 80-100 days. Subsequent, laboratory degradation experiments performed with aquifer material from the different parts of the aquifer found correlations between previous exposure to the phenoxy acids (MCPP and dichlorprop) and the amount of phenoxy acids degraded after 50 days of incubation. A correlation was also found between the amount of exposure and the number of specific phenoxy acid degrading bacteria. Furthermore the presence of genes involved in phenoxy acid degradation was only found within the previously exposed part of the aquifer. Modeling of the degradation curves was only successful using a growth degradation kinetic model. All these results combined indicate, that the injection of low concentrations of
phen oxy acids resulted in a proliferation of specific microorganisms and thus an enhanced degradation potential in the previously exposed part of the aquifer.

Natural attenuation was evaluated as a remedial action at the Sjoelund landfill, where phenoxy acids contaminate the groundwater (up to 65 µg/L). Close to the landfill anaerobic conditions prevail, likely due to degradation of mg/L concentrations of other organic compounds in the thick unsaturated zone below the landfill. Mixing in the plume with aerobic infiltrating water from the unsaturated zone gradually increases the oxygen concentration with distance from the landfill. Flux calculations, findings of putative phenoxy acid metabolites, and laboratory degradation experiments using aquifer material from the site, all indicated that aerobic degradation of the phenoxy acids was an important process in the aquifer. Thus it was concluded that natural attenuation was a viable remediation option at the site.

Many herbicide point source sites are anaerobic and phenoxy acids are not easily degraded under anaerobic conditions. Experiments were conducted using aquifer material from two anaerobic herbicide point source sites (a machine pool and an old landfill) in order to study the potential for stimulating biodegradation of phenoxy acids by addition of oxygen. A positive effect on biodegradation was observed even at relatively low oxygen concentrations (2 mg/L) indicating that biostimulation could be a feasible remediation technology for phenoxy acids in anaerobic aquifers.

Little research has investigated in situ remediation technologies for herbicides. In contrast, several technologies have been developed for ex situ treatment of herbicides. Based on the knowledge of the processes governing the fate of the herbicides in groundwater and the success rates of the ex situ technologies, an assessment of the viability of the different in situ technologies was made.

Technologies based on volatilization (such as the thermal technologies and airsparging) were ruled out as potential technologies due to the high water solubility and the low vapor pressure of the selected herbicides. Pump and treat and phytoremediation could potentially be used (depending upon the hydrogeology of the aquifer), because of the high mobility of the herbicides in aquifers and plants. Chemical oxidation and reduction technologies were also seen as viable, however, in many cases these must be used in conjunction with other treatments in order to completely mineralize the target herbicides. Bioremediation was found to be an attractive remedial option for the more degradable herbicides - mainly the phenoxy acids.

In general, the experiments conducted and the literature reviewed suggest that a number of different in situ technologies exist, which could be feasible to remediate groundwater contaminated by herbicides from point sources. However, knowledge is required regarding risk assessments of the different types of point sources in order to focus future remediation initiatives.
Dansk resumé


Denne afhandling består af en sammenfatning af emnet ”*In situ* bioremediering af grundvand forurenet med herbicider fra punktkilder” samt 7 artikler, der dækker det eksperimentelle arbejde udført under PhD projektet.

En væsentlig del af pesticidfundene i grundvand stammer sandsynligvis fra punktkilder såsom gamle lossepladser, maskinstationer, gartnerier og spild. Karakteristisk for punktkilder er, at relativt høje koncentrationer findes i en begrænset mængde vand. Disse karakteristika gør det relevant at vurdere afværgetiltag i forhold til pesticidforurenet grundvand fra punktkilder.

Otte af de mest anvendte og oftest fundne pesticider (allesammen herbicider) blev udvalgt til denne undersøgelse. De valgte herbicider, der tilhører forskellige grupper af herbicider, var MCPP (mecoprop), dichlorprop, 2,4-D, DNOC, isoproturon, atrazin, BAM (en metabolit fra chlortiamid og dichlobenil) og bentazon.

Sorption af de 8 udvalgte herbicider var begrænset i de undersøgte og refererede sandede akviferer. Retardationskoefficienter varierede mellem 1 og 3 for phenoxy-syrerne (MCPP, dichlorprop og 2,4-D), BAM og bentazon. Sorption af isoproturon, atrazin og DNOC var en anelse højere i akviferer med relativt højt organisk kulstof indhold eller lav pH, resulterende i retardationskoefficienter på op til 10. Kun den neutrale del af den svage syre DNOC blev sorberet, og derfor var retardationskoefficienten meget afhængig af pH.


Et feltinjektionsforsøg blev udført in en overfladenær sandet akvifer. De to injicerede phenoxy-syrer MCPP og dichlorprop (40 µg/L hver) blev hurtigt nedbrudt efter en lagperiode på 80-100 dage. Efterfølgende laboratorieforsøg med sediment og grundvand fra forskellige steder i akviferen fandt en korrelation mellem den tidligere eksponering til phenoxy-syrerne og mængden af phenoxy-syrer nedbrudt efter 50 dages inkubation. En korrelation blev også fundet mellem mængden af eksponering og antallet af specifikke phenoxy-syrenedbrydende mikroorganismer. Desuden blev gener, involveret i

Naturlig nedbrydning blev evalueret som afværgeteknologi på Sjølund losseplads, hvor phenoxyssyrer har forurenet grundvandet (op til 65 µg/L). Der er anaerobe forhold tæt ved lossepladsen, sandsynligvis pga. nedbrydning af mg/L-koncentrationer af andre organiske stoffer i den tykke umættede zone under lossepladsen. Pga. opblanding med aerobt vand fra den umættede zone nedstrøms lossepladsen, øges itkonzentrationen i grundvandet med stigende afstand fra lossepladsen. Fluxudregninger, tilstedeværelse af mulige nedbrydningsprodukter samt laboratorienedbrydningsforsøg med sediment og grundvand fra akviferen tydede alle på, at aerob nedbrydning af phenoxyssyrerne var en vigtig proces. Det blev derfor konkluderet, at naturlig nedbrydning kunne anvendes som afværetiltag på lokaliteten.

Mange herbicidpunktkilder er anaerobe, og phenoxyssyrer er ikke letnedbrydelige under anaerobe forhold. Ekspitioner blev derfor udført med akvifermateriale fra to anaerobe herbicidpunktkilder (en maskinstation og en gammel losseplads) for at vurdere potentialet for at stimulere bionedbrydningen af phenoxyssyrer ved at tilsætte itl. En positiv effekt på bionedbrydningen blev observeret ved relativt lave itkonzentrationer (2 mg/L), hvilket indikerer at biostimulering kan være en mulig afværgeteknologi for phenoxyssyrer i anaerobe akviferer.

Kun meget lidt forskning har fokuseret på in situ afværgeteknologier for herbicider. I modsætning hertil er der blevet udviklet mere teknologier til ex situ behandling af herbicider med størst fokus på spildevand fra fabrikker, der producerer herbicider. Baseret på succesraterne fra disse teknologier og på viden om de processer, der bestemmer skæbnen af herbicider i grundvand, blev en række in situ afværgeteknologiers potentiale vurderet.

Overordnet set tyder de udførte eksperimentelle forsøg og litteraturgennemgangen på, at der eksisterer mange forskellige *in situ* teknologier, der kan anvendes til at afværge grundvand forurenset med pesticider fra punktkilder. Det er dog nødvendigt at øge den aktuelle viden vedrørende risikovurderinger af de forskellige typer af punktkilder, for at fokusere den fremtidige afværgeindsats.
1. Introduction

In many countries, the drinking water supply is based primarily on groundwater, and protection of this resource is therefore a matter of great concern. In contrast to practices in many other countries, groundwater in Denmark undergoes only simple treatment such as filtration and aeration before delivery to consumers. This requires high quality groundwater, meaning that groundwater must meet drinking water quality guidelines with respect to e.g. maximum allowed concentrations of xenobiotics.

Approximately two thirds of the area of Denmark is used for agricultural purposes, which in most cases, implies the use of pesticides. Since the 1950’s the amount of pesticides sold in Denmark has increased significantly including more than 500 different pesticide products (Figure 1). Over the last 10 years, however, the quantity has decreased due to restrictions and the introduction of low-dose products. The groundwater extracted for drinking water in Denmark is on average 30-40 years old, which means that the pesticide problems we encounter today may only be the tip of the iceberg, and that the expected positive effects on groundwater quality due to the recent decreases in pesticide use will not be seen for years to come.

**Figure 1. Pesticides sold in Denmark 1955-1999. From (GEUS, 2000).**

Since 1993, there have been three systematic programs to monitor pesticides in Danish groundwater: GRUMO (groundwater monitoring wells covering all major groundwater types in Denmark), LOOP (very shallow wells located under agricultural fields) and the monitoring program at the waterworks. Initially 8 different pesticides were monitored for, whereas today’s program covers more than 50 pesticides. This increase in the number of pesticides analyses has resulted in an increase in the number of findings. Compared to the total quantity of pesticides used, it may be expected, that only a fraction of the actual groundwater contaminations has been found.

The percentage of groundwater samples where pesticides have been detected is high in all monitoring programs (Table 1). Furthermore, more than 10 % of the groundwater in all monitoring programs contains pesticides above the maximum contaminant level
(MCL) which is 0.1 μg/L in EU (EEC, 1980). These numbers prove that the use of pesticides has a substantial effect on the groundwater quality.

**Table 1. Findings of pesticides in Danish monitoring programs 1993-2000 (GEUS, 2001).**

<table>
<thead>
<tr>
<th>Monitoring Program</th>
<th>GRUMO</th>
<th>LOOP</th>
<th>Waterworks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Findings (%)</td>
<td>36</td>
<td>60</td>
<td>26</td>
</tr>
<tr>
<td>Findings &gt; 0.1 μg/L (%)</td>
<td>12</td>
<td>20</td>
<td>10</td>
</tr>
</tbody>
</table>

The frequent findings of pesticides in Danish groundwater has resulted in the closure of many drinking water wells. Since 1994, the presence of pesticides has been the major reason for closure of drinking water wells decommissioned due to contamination (Figure 2).

![Figure 2. Number of closed abstraction wells in Denmark 1987-1997. From (HOH, 1998).](image)

Pesticides are also used heavily in other agricultural countries and several international monitoring programs for pesticides have shown similar frequencies of detections in the groundwater (Walls et al., 1996; Kolpin et al., 2000; Barbash et al., 2001; European Environment Agency, 2002). However, the frequency of groundwater samples where the pesticide concentrations exceed the MCL is lower. This is due to differences in water quality standards among the countries. The MCL in EU countries reflect the policy that pesticides should not be detected in groundwater and therefore the MCL’s correspond to the analytical limit (0.1 μg/L corresponds to the detection limit in 1980). In contrast, the American MCL’s are determined based on a combination of toxicological evaluations and considerations regarding best available treatment technology and costs. Thus, American MCL’s are up to 7000 times higher than the EU
MCL’s (US EPA, 2001). Additionally, the American MCL’s are determined individually for each pesticide resulting in huge variations in MCL’s – for example glyphosate: 700 µg/L, 2,4-D: 70 µg/L, atrazine: 3 µg/L, and lindane: 0.2 µg/L (US EPA, 2001). Additionally, there are pesticides for which no MCL has been determined. Guidelines for pesticide degradation products are also rare, even though a survey of groundwater in Iowa in 1995-1998 by the United States Geological Survey showed eight out of the ten most common herbicides were present as degradation products (Kolpin et al., 2000).

Table 2. The 10 most frequently found pesticides in all monitoring programs in United States, Europe, and Denmark. In each monitoring program, the pesticides were ranked after frequency (i.e. the most frequently found pesticide was ranked 1 etc.) and the average frequency was calculated as the summed frequencies in each monitoring program divided by the number of monitoring programs. Modified after (Brüsh and Felding, 2000).

<table>
<thead>
<tr>
<th>Pesticide</th>
<th>United States Average frequency</th>
<th>Europe (excl. DK) Average frequency</th>
<th>Denmark Average frequency</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atrazine</td>
<td>1.3</td>
<td>Atrazine</td>
<td>BAM</td>
</tr>
<tr>
<td>Atrazine, deethyl</td>
<td>2.5</td>
<td>Atrazine, deethyl</td>
<td>Atrazine, deethyl</td>
</tr>
<tr>
<td>Simazine</td>
<td>3</td>
<td>BAM</td>
<td>Atrazine, deisopropyl</td>
</tr>
<tr>
<td>Prometon</td>
<td>3.8</td>
<td>Bentazone</td>
<td>Atrazine</td>
</tr>
<tr>
<td>Metolachlor</td>
<td>5</td>
<td>Simazine</td>
<td>Bentazone</td>
</tr>
<tr>
<td>Tebuthiuron</td>
<td>6.5</td>
<td>Diuron</td>
<td>MCPP</td>
</tr>
<tr>
<td>Alachlor</td>
<td>8.3</td>
<td>Isoproturon</td>
<td>Dichlorprop</td>
</tr>
<tr>
<td>Carbofuran</td>
<td>9.3</td>
<td>Atrazine, deisopropyl</td>
<td>MCPA</td>
</tr>
<tr>
<td>Cyanazine</td>
<td>9.3</td>
<td>MCPP</td>
<td>Simazine</td>
</tr>
<tr>
<td>Metribuzine</td>
<td>10.3</td>
<td>Dichlorprop</td>
<td>Atrazine, hydroxy</td>
</tr>
</tbody>
</table>
Many different pesticides belonging to many different chemical groups with varying properties have been found in the groundwater. However, most findings are related to one of 7 groups and all of them are herbicides (Table 2). The difference between the pesticide contamination found in Europe and in USA is primarily due to the differences in pesticides use. In Denmark, BAM (the degradation product from dichlobenil or chlortiamid) is the most frequently detected herbicide. Additionally, the group of triazines and phenoxy acids and the herbicide bentazone are frequently found.

Numerous sources of groundwater contamination with pesticides exist. In addition to diffuse sources caused by leaching from agricultural areas, recent investigations indicate that point sources contribute significantly (Helweg, 1994; Gintautas et al., 1992; Baun et al., 2002; Jørgensen et al., 2000; Helweg, 2002; Comfort et al., 2001; AVJ, 2002; Frede et al., 1998; Helweg et al., 1999). Point sources are characterized by relatively high pesticide concentration in a limited amount of water. This characteristic makes assessment of remedial actions towards pesticides in groundwater from point sources relevant.

A number of different in situ remediation technologies based on various processes such as sorption, degradation and volatilization exist, and numerous references exist regarding successful application in the cases of e.g. BTEX or chlorinated solvents plumes. However, knowledge regarding pesticide remediation is scarce. Because pesticides as a group are very heterogeneous in terms of physical and chemical properties, the success of a given remediation technology will depend greatly on the pesticide in question, of the type of source, and of the aquifer in question. Potentially numerous small pesticide point sources exist. Therefore, inexpensive technologies have the greatest potential. Bioremediation technologies are among the less expensive remediation technologies (Cookson, 1995), and also have the advantage that they are based on processes which are already occurring in the environment, and thus minimize disturbance of the site.

In summary, the extensive use of pesticides in agricultural countries and the subsequent findings of such compounds in the groundwater reveal the need for initiatives designed to limit the threat to drinking water resources. Since a significant part of the pesticide contamination arises from numerous point sources, development of in situ bioremediation technologies appears to be beneficial. Before remediation technologies can be applied, there is need for a thorough understanding of the processes that control the fate of each pesticide in aquifers.

This thesis focuses mainly on 8 herbicides used as model compounds: MCPP (mecoprop), dichlorprop, 2,4-D, DNOC, isoproturon, atrazine, BAM (a metabolite of the herbicides chlortiamid and dichlobenil), and bentazone. All compounds are herbicides, and were selected because they are among the most frequently found
pesticides in groundwater. This is probably partly because these herbicides have constituted a major part of pesticide sales and partly due to their high mobility.

The objectives of the thesis were: (A) to obtain detailed knowledge about relevant characteristics (transport, sorption, and degradation) of 8 selected herbicides in aquifers; (B) to get an overview of the published literature regarding in situ remediation technologies for the 8 selected herbicides; (C) to assess via laboratory and field studies natural attenuation and stimulated biodegradation of phenoxy acids in aquifers.

Thesis delimitation. The main focus of the thesis is on in situ bioremediation of the 8 selected herbicides in sandy aquifers. In order to get a better overview, a literature review of other in situ remediation technologies was included. Occasionally, results for other pesticides and fate of the selected herbicides in other environments (chalk aquifers, soil, and wastewater) were included in the thesis as well. Additionally, results obtained from on site and ex situ remediation technologies were cited, when the number of in situ references was limited. The focus in this thesis is on smaller point sources (for instance from landfills or machine pools) whereas large pesticide point sources from, for instance chemical plants, are not discussed.
2. Point sources

Numerous smaller point sources can arise where herbicides have been handled and disposed of. Whereas landfill leachate plumes have been intensively studied the last decade (Christensen et al., 2001), only scarce knowledge exists regarding other herbicide point sources.

Herbicides have been found in many leachates, and in groundwater downgradient from many old landfills, herbicides are among the critical compounds (Christensen et al., 2000b). Typical herbicide concentrations in groundwater from landfills are 10-250 µg/L (Gintautas et al., 1992; Lyngkilde and Christensen, 1992; Zipper et al., 1998; Baun et al., 2002). Although the leaching strength from landfills often varies in time and space, a landfill will be a continuous source over a longer timeframe (Kjeldsen et al., 1998). Generally other organic carbon compounds will be present close to a landfill, typically in mg/L concentrations. Degradation of these organic compounds will sequentially consume the electron donors present and lead to the formation of redox zones (Christensen et al., 2000a) These characteristics are important to consider when remediation options are being examined.

A number of other potential point sources have been suggested in the literature including machine pools, market gardens, roads, and railways (Helweg, 1994; Jørgensen et al., 2000; Bastrup, 2001; AVJ, 2002; Bay and Hansen, 2001; Frede et al., 1998; Helweg et al., 1999) (see Figure 3).

Figure 3. Potential pesticide point sources. From (Helweg, 1994).
Point sources are created by accidental spills, incorrect handling of spraying equipment, inexpedient disposal of waste, or excessive use in vulnerable areas. The number of such potential point sources exceeds 100,000 in Denmark alone (based on the number of farms, machine pools and market gardens) (Danmarks Statistik, 2001). Recently, the Danish organisation “Amternes Videnscenter for Jordforurening” conducted an investigation to identify pesticide point sources in the counties in Denmark (AVJ, 2002). Pesticides were detected at 93% of the 145 investigated locations and the MCL of 0.1 µg/L in groundwater was exceeded in 70% of the cases. Very high concentrations (10-1000 µg/L) were found at 8% of the sites. In total, more than 90 different pesticides were detected, and often more than one pesticide was found at each site. No general conclusions could be made regarding occurrences of contaminants, leaching, spreading, or redox conditions at the sites.

At many of the abovementioned point source sites the pesticides are present locally at very high concentrations considering that water supply wells are closed when the pesticide content exceeds 0.1 µg/L. Therefore, assessments of remedial actions at the sites are relevant in order to prevent the contamination reaching water supply wells.

It is difficult to quantify what fraction of the groundwater pesticide contamination originates from point sources and how much is due to leaching from normal agricultural practices. One way of distinguishing between these two is to attribute “high” pesticide concentrations to point sources. In the following a “high” pesticide concentration is defined as being above 0.5 µg/L since the highest concentration in well screens underneath fields where pesticide use was in compliance with approved practices (in the period 1991-1998) was 0.3 µg/L (Tuxen et al., 2001). It should be emphasized that the value of 0.5 µg/L is only an operational value and not scientifically proven. During the period 1991-1998 a total of 6708 screens were analyzed for pesticides in the Danish monitoring program and a total of 1609 finds were made (GEUS, 1999). A search in the databases (kindly provided by The Geological Survey of Denmark and Greenland) revealed that 12% of these findings could be attributed to point sources assuming a threshold value of 0.5 µg/L (Figure 4).

![Figure 4. Distribution of pesticide concentrations >0.5 µg/L, >0.1 µg/L, and <0.1 µg/L in the Danish monitoring program 1991-1998. Based on data from (GEUS, 1999).](image-url)
This number is probably too low an estimate, since originally high-concentrated point sources are being diluted substantially during the transportation to the monitoring wells and inside the wells. Using a threshold value of 0.1 μg/L results in 38% of the findings coming from point sources (Figure 4). Although such calculations are not scientifically rigorous, the results strongly suggest that point sources contribute significantly to herbicide contamination in Danish groundwater. This is likely also the case in other countries.
3. Fate of herbicides in groundwater

Understanding the fate of each of the 8 selected herbicides in groundwater forms the basis for the subsequent assessment of potential remediation technologies. The fate is controlled by several processes which are dependent on the physicochemical properties of the individual herbicides as well as on the aquifer characteristics.

3.1 Aquifer characteristics

The temperature in shallow, Danish aquifers is typically in the range of 8-12 ºC and the pH is generally between 5 and 8 (Bjerg and Christensen, 1992; Pedersen, 2000; Tuxen et al., VII, 2002). In pristine sandy aquifers the organic carbon content is usually low, with total organic carbon concentrations of about 1-4 mg/L in the groundwater and organic carbon fractions in the sediment of 0.01-0.48 % (Pedersen et al., 1991; Christensen et al., 1996). The concentrations of nutrients are low in uncontaminated aquifers making the environment oligotrophic.

The numbers of microorganisms present in the aquifers are orders of magnitudes lower than for instance in the top soil (typically in the range of 10^2-10^4 cells/mL groundwater and 10^3-10^6 cells/g sediment) (Albrechtsen and Winding, 1992; Ghiorse and Wilson, 1988; Dobbins et al., 1992). Accordingly, 97-100% of the microbial biomass is attached to the sediment phase (Harvey et al., 1984).

In uncontaminated aquifers, oxygen is usually present in the upper layers due to the infiltrating aerobic rainwater, but with increasing depth other compounds generally take over as the primary electron acceptor (Pedersen, 2000; Appelo and Postma, 1996; Pedersen et al., 1991). At many herbicide point source sites the redox conditions are anaerobic close to the source (Tuxen et al., VII, 2002; Tuxen et al., VI, 2002). Usually, this is not attributed to oxygen consumption by herbicides (present in µg/L) but rather to degradation of compounds such as ammonium and non-volatile organic carbon (NVOC) present in the point sources in mg/L concentrations.

3.2 Transport and fate processes

The most important processes that determine the fate of herbicides in groundwater are transport, sorption and degradation. Volatilization is not included in the list, because this process is only considered to be significant for compounds with a Henry’s constant (defined as the partial pressure of the compound in the air divided by the concentration in the water phase) above 10^-5 atm⋅m^3/mole (Barbash and Resek, 1996). The selected herbicides all have Henry’s constants below 10^-7 atm⋅m^3/mole.

The transport of the dissolved herbicides in the saturated zone of aquifers is controlled by advection and dispersion (Freeze and Cherry, 1979). These processes are strongly dependent on the geological properties of the aquifers – especially spatial variability in
hydraulic conductivities. Whereas description of herbicide transport in homogeneous aquifers is relatively simple, the transport process in heterogeneous aquifers is quite complicated. This is due to the occurrences of other processes, such as preferential flow and diffusion into the sediment matrix – processes that enhance and limit the transport, respectively. An understanding of these processes with respect to herbicides is limited, but modeling exercises have shown that it was necessary to include preferential flow in order to describe findings of BAM under a clayey till cover (Kistrup and Jørgensen, 2001). As well, inclusion of matrix diffusion was necessary to describe atrazine breakthrough curves in a column experiment (Yiacoumi and Tien, 1994). Preliminary experimental results suggest that for a number of pesticides, matrix diffusion is a significant process in clayey till (Broholm, 2002). Another complicating process may be facilitated transport, where the herbicides are sorbed to colloids transported with the groundwater. This process has been shown to enhance the transport of organochlorine pesticides significantly (Ding and Wu, 1997).

Sorption is the process by which herbicides become associated with the solid matrix. In this thesis it will be quantified by $K_d$-values (defined as the sorbed concentration divided by the aqueous concentration) determined assuming a linear sorption isotherm, which has been shown to be valid for $\mu g/L$ concentrations (Karickhoff, 1984). Corresponding retardation factors, $R$, will also be presented - defined as the travel velocity of the herbicide divided by the groundwater velocity, and estimated using the formula: $R = 1 + \frac{\rho_b}{\varepsilon} \cdot K_d$, where $\rho_b$ is the bulk density of the sediment and $\varepsilon$ is the porosity. Sorption causes retardation of the herbicide transport compared to groundwater flow. Different herbicides are, depending upon their physico-chemical properties and the sorption mechanisms involved, retarded differently resulting in separation of the herbicides in the aquifers. Additionally, sorption is expected to influence degradation of herbicides, because only the dissolved fraction of the herbicides is expected to be available for microorganisms (Mihelcic et al., 1993; Scow et al., 1995). The extent to which sorption occurs in aquifers is expected to be limited compared to topsoil, primarily due to the lower organic carbon content. However, sorption mechanisms other than the hydrophobic partitioning process (which is dominating in topsoil) and which are not related to the organic carbon content may occur. These mechanisms will be dependent upon the herbicide in question (section 3.3).

Herbicide degradation processes may be microbially mediated or abiotic. This thesis will mainly focus on biodegradation, which is considered to occur most frequently (Helweg, 1983; Topp et al., 1997). In contrast to transport and sorption processes, degradation transforms the herbicides into other compounds. In the case of mineralization the herbicides are transformed completely to $CO_2$, $H_2O$ and inorganic
salts. Several different degradation processes, such as oxidative, reductive and hydrolytic processes, are known (Topp et al., 1997). The extent to which these processes will occur is dependent on a number of aquifer and herbicide characteristics. In general, degradation of herbicides in aquifers is expected to occur at low rates or after long lag phases compared to degradation in topsoil. This is attributable to lower temperature and smaller microbial biomasses in aquifers.

3.3 Fate of selected herbicides

<table>
<thead>
<tr>
<th>Chemical name</th>
<th>Formula and molecular weight (g/mol)</th>
<th>Structure formula</th>
<th>Solubility (mg/l)</th>
<th>log $K_{ow}$</th>
<th>$pK_a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>MCPP*-(+)-2,4-dichloro-2-methylphenoxo) propanoic acid</td>
<td>$C_{10}H_9ClO_3$ 214.6</td>
<td><img src="image" alt="Structure" /></td>
<td>734 (25 °C)</td>
<td>1.26</td>
<td>3.78</td>
</tr>
<tr>
<td>Dichlorprop*-(+)-2,4-dichlorophenoxy) propanoic acid</td>
<td>$C_{10}H_9ClO_3$ 235.1</td>
<td><img src="image" alt="Structure" /></td>
<td>350 (20 °C)</td>
<td>1.77</td>
<td>3.00</td>
</tr>
<tr>
<td>2,4-D*-(2,4-dichlorophenoxy) acetic acid</td>
<td>$C_9H_8ClO_3$ 221.0</td>
<td><img src="image" alt="Structure" /></td>
<td>311 (25 °C, pH 1)</td>
<td>2.6-2.8</td>
<td>2.64</td>
</tr>
<tr>
<td>DNOC*--2-methyl-4,6-dinitrophenol</td>
<td>$C_{12}H_7NO_4$ 198.1</td>
<td><img src="image" alt="Structure" /></td>
<td>130 (15 °C)</td>
<td>2.12$^b$</td>
<td>4.31$^b$</td>
</tr>
<tr>
<td>Isoproturon*--N,N-dimethyl-N-(4-[1-methyl-ethyl]phenyl) urea</td>
<td>$C_{10}H_7N_2O$ 206.3</td>
<td><img src="image" alt="Structure" /></td>
<td>65 (22 °C)</td>
<td>2.5</td>
<td>$\sim$</td>
</tr>
<tr>
<td>Atrazine*--6-chloro-N,N,N,N'-tetraethyl-1,3,5-triazine-2,4-diamine</td>
<td>$C_{12}H_8ClN_3$ 215.7</td>
<td><img src="image" alt="Structure" /></td>
<td>33 (22 °C)</td>
<td>2.5</td>
<td>1.7</td>
</tr>
<tr>
<td>Bentazon*--3-(1-methyl-ethyl)-1H-2,1,3-benzothiadiazin-4(3H)-one-2,2-dioxide</td>
<td>$C_{10}H_7ClNO_S$ 240.3</td>
<td><img src="image" alt="Structure" /></td>
<td>570 (22 °C)</td>
<td>0.77 (pH 5) - 0.46 (pH 7)</td>
<td>3.3</td>
</tr>
<tr>
<td>BAM*--2,6-dichlorobenzamide</td>
<td>$C_7H_5ClNO$ 201.0</td>
<td><img src="image" alt="Structure" /></td>
<td>nf$^c$</td>
<td>0.77</td>
<td>$\sim$</td>
</tr>
</tbody>
</table>

$^a$ (Tomlin, 1997)
$^b$ (Schwarzenbach et al., 1988)
$^c$ Not relevant
$^d$ (Nakagawa et al., 1992)
$^e$ nf: Not found
3.3.1 Phenoxy acids

Three of the selected herbicides, MCPP (mecoprop), dichlorprop, and 2,4-D belong to the group of phenoxy acids, and because they have very similar chemical structures and physico-chemical properties (Table 3) they will be discussed together. Phenoxy acids have, for many years, been the dominant group of herbicides used in Denmark. Presently, however, only restricted application of these compounds is permitted.

Sorption of phenoxy acids in aquifers has been found to be limited, with \( K_d \)-values ranging from 0 to 0.26 L/kg (Agertved et al., 1992; Broholm et al., I, 2001; Madsen et al., 2000; Rügge et al., 1999a; Tuxen et al., 2000; Kristensen et al., 2001a) (Figure 5). The reported \( K_d \)-values correspond to retardation factors of 1-2.5. In one investigation the \( K_d \)-value of the phenoxy acids was negatively correlated with the pH value of the groundwater (Madsen et al., 2000). The low sorption and the correlation with pH was probably caused by the almost complete dissociation of the compounds at the investigated pH-values due to their low pK\(_a\)-values of 2.6-3.8. Dissociated compounds are extremely water soluble and thus not susceptible to hydrophobic partitioning with the organic fraction of the sediment (Schwarzenbach et al., 1993). The observed sorption, although limited, must therefore, be governed by other sorption mechanisms. Studies of sorption mechanisms of phenoxy acids suggest that electrostatic interactions (in some cases combined with exchange reactions with ligands) between the negatively charged carboxyl-groups in the dissociated fraction and positively charged sites on the investigated minerals and iron oxides were significant (Clausen et al., 2001; Clausen and Fabricius, 2001). This sorption mechanism was, according to the theory, found to be greatest on surfaces with high points of zero charge (PZC) such as calcite and iron hydroxides.

![Breakthrough curves of the phenoxy acids MCPP and dichlorprop and the tracer bromide in a field injection experiment in an aerobic, sandy aquifer. From (Broholm et al., I, 2001).](image-url)
Degradation. Numerous studies of phenoxy acid degradation in aquifers (limestone as well as clastic) have been reported in the literature (Kristensen et al., 2001b; Agertved et al., 1992; Broholm et al., I, 2001; Klint et al., 1993; Williams et al., 2001; Heron and Christensen, 1992; Tuxen et al., 2000). In general, the three selected phenoxy acids were degraded to the same extent and at comparable rates, likely because most bacterial phenoxy acid degraders are capable of transforming several phenoxy acids (de Lipthay et al., IV, 2002; Tuxen et al., III, 2002; Kilpi, 1980). In most of the aerobic experiments the phenoxy acids were degraded, although recalcitrance was observed in some aquifers (Johnson et al., 2000; Pedersen, 2000). In contrast, recalcitrance of the phenoxy acids was observed in all anaerobic aquifers, except in single microcosms in two recent studies (Tuxen et al., VII, 2002; Tuxen et al., VI, 2002). In all reported experiments lag phases of various lengths preceded degradation (see example in Figure 5), possibly due to a combination of gene transfer, induction of enzyme activity and growth of specific degraders (Tuxen et al., III, 2002; de Lipthay et al., IV, 2002). To date, no literature could be found regarding degradation pathways of phenoxy acids under aquifer conditions. However, it could be speculated that they are similar to the degradation pathways reported from topsoil experiments. For several of the investigations this implies pure cultures. When phenoxy acids are degraded under aerobic conditions the corresponding chlorophenols are formed as intermediates (e.g. (Oh and Touvinen, 1991; Smith, 1985a; Smith, 1985b; Smith et al., 1994; Tett et al., 1994). These chlorophenols are subsequently further degraded and eventually, large fractions of the compounds are mineralized. Anaerobic dechlorination of 2,4-D can occur with production of 4-chlorophenoxyacetic acid (Boyle et al., 1999) and a similar degradation pathway can thus be postulated for MCPP and dichlorprop.

3.3.2 DNOC
The herbicide DNOC belongs to the group of nitroaromatic compounds and is one of the so-called yellow herbicides (Table 3). Nitroaromatic herbicides have been used extensively as non-selective herbicides and are among the most toxic compounds that have been commonly applied in Denmark in the past (Jensen, 1966).

Sorption. Investigations of the magnitude of the DNOC sorption in aquifers revealed surprisingly high and varying $K_d$-values (from 0.1 to to 0.98 L/kg, corresponding to retardation factors of approximately 1.5 to 6) compared to what was expected from the $K_{ow}$ of the compound and the large degree of dissociation at the investigated pH-values (Broholm et al., II, 2001; Tuxen et al., 2000). Hence, hydrophobic partitioning of
DNOC to organic matter appears to be negligible, relative to other sorption mechanisms. Investigations by (Haderlein and Schwarzenbach, 1993) and (Weissmahr et al., 1997) suggest that nitroaromatic compounds may be bound by a EDA complex formation between siloxane oxygen’s of the clays and the nitroaromatic substituents. This sorption mechanism is of particular importance for DNOC as it contains two nitro groups, which enhance the electron-withdrawing and electron-delocalizing properties, and thereby enhance sorption. However, recent investigations question the formation of EDA complexes as the explanation for the observed sorption and suggest a more non-specific sorption mechanism involving direct interaction between the nitrogroups and inter- or outerlayer cations in the clay (Pelmenschikov and Leszczynski, 1999; Johnston et al., 2001; Boyd et al., 2001). In a field investigation the $K_d$-value varied spatially an order of magnitude and was, to some extent, negatively correlated with pH (Broholm et al., II, 2001). Additionally, batch experiments with manipulated pH’s (ranging from 2.7 to 6.5) revealed a linear relationship between $K_d$ and the neutral fraction of DNOC indicating that the sorption of the dissociated fraction was negligible (Figure 6). However, variations in pH alone could not explain the spatially varying $K_d$-values of DNOC. (Weissmahr et al., 1999) demonstrated that the equivalent fraction of specific cations on the clay mineral surfaces had significant effects on sorption. However, such an effect was not found to be of importance for the groundwater in the Vejen aquifer (Broholm et al., II, 2001). Instead, variations in clay content were suggested as an additional explanation for the sorption variability in the Vejen aquifer.

Figure 6. $K_d$ for DNOC in aquifer sample suspension with adjusted pH. (a) $K_d$ as a function of the neutral fraction of DNOC. The solid line is a linear regression to the data. (b) $K_d$ as a function of pH in the aquifer samples. The solid line is the regression line from (a). From (Broholm et al., II, 2001).
Degradation. DNOC degradation studies have been performed in both aerobic and anaerobic aquifers. Whereas all anaerobic studies showed rapid degradation (Arildskov et al., 2001; Pedersen, 2000), degradation was only observed in some of the aerobic studies (Rügge et al., 2000; Tuxen et al., 2000; Broholm et al., II, 2001; Tuxen et al., III, 2002; Pedersen, 2000) (Figure 7). The rapid degradation in the anaerobic studies were proven to be abiotic and it was speculated that the nitro-groups were reduced to amines forming diamino-cresol – similar to what has been reported for other nitroaromatic compounds in aquifers (Arildskov et al., 2001; Pedersen, 2000). The varying degradation potential in aerobic aquifers, even within each investigation, is more complex and not fully understood. In one of the investigations (Rügge et al., 1999b) amendment with nutrients enhanced degradation, in another investigation (Tuxen et al., III, 2002) the degree of pre-exposure seemed to have an effect, and in a third investigation there was speculation regarding the potential for pH effects (Broholm et al., I, 2001).

![Figure 7](image-url)  
Figure 7. Aerobic recalcitrance and abiotic anaerobic degradation of DNOC in a sandy aquifer. Modified after Pedersen (2000)(Pedersen, 2000).

3.3.3 Isoproturon
Isoproturon belongs to the group of phenylurea herbicides (Table 3). It is used for weed control for spring and autumn sown cereals. The herbicide entered in Danish market in 1976 and since then, its use has increased.

Sorption. Studies of sorption of isoproturon in aquifers revealed $K_d$-values in the range of 0.03 to 0.85 L/kg corresponding to retardation factors of approximately 1.2-6 (Tuxen et al., 2000; Broholm et al., I, 2001; Madsen et al., 2000; Johnson et al., 1998). One example of the delayed breakthrough of isoproturon is shown in Figure 8. (Madsen et al., 2000) found a positive correlation of $K_d$ with the sediment surface area and the organic carbon content comparable to the results of (Rae et al., 1998). The influence of
the organic carbon content on sorption indicates the sorption process to be partly hydrophobic. The sorption studies by (Clausen et al., 2001; Clausen and Fabricius, 2001), suggest that the positive influence of surface area is more likely connected to the clay content than to the iron oxides, and that the sorption is governed by van der Waals forces. Sorption to calcite was found to be insignificant (Clausen et al., 2001) thus supporting the suggestion that the significant sorption in a chalk aquifer was attributable to small quantities of organic matter or clay located in fractures in the chalk, whereas the chalk matrix itself was relatively inert (Johnson et al., 1998).

Figure 8. Breakthrough curve of isoproturon and the tracer bromide in a column experiment with aquifer material from an aerobic, sandy aquifer. From (Tuxen et al., 2000).

**Degradation.** Investigations in aerobic chalk aquifers have revealed a potential for isoproturon degradation (Kristensen et al., 2001a; Johnson et al., 1998; Johnson et al., 2000). The metabolite monodesmethyl-isoproturon was identified, but not further degraded. This is in accordance with the findings of (Kristensen et al., 2001b) who observed a very limited evolution of $^{14}$CO$_2$ originating from $^{14}$C-isoproturon in a chalk aquifer. No studies conducted in sandy aquifers have observed degradation of isoproturon (Pedersen, 2000; Tuxen et al., III, 2002; Broholm et al., I, 2001; Larsen et al., 2000; Skark and Obermann, 1995; Larsen and Aamand, 2001) whether under aerobic or under anaerobic conditions (Figure 8). In contrast, isoproturon has been found to be readily degradable in topsoils (e.g. (Pieuchot et al., 1996; Cox et al., 1996)).
3.3.4 Atrazine

Atrazine is an herbicide in the triazine family (Table 3). Atrazine is one of the most commonly-used herbicides worldwide and has been the subject of numerous investigations. It is used for weed control in Christmas tree plantations, corn fields, and broad-spectrum weed control on bare soil. It was used for the first time in Denmark in 1960 with increasing sales over the years until it was banned in 1994 due to numerous findings of the compound and related metabolites in the groundwater.

**Sorption** of atrazine in sediments has been investigated in several studies. The reported $K_d$-values range from approximately 0 to 1.8 L/kg corresponding to retardation factors of 1 to 10 (Madsen et al., 2000; Seybold et al., 1994; Roy and Krapac, 1994; Rügge et al., 1999a; Widmer and Spalding, 1995; Agertved et al., 1992; Xu et al., 1999; Pedersen, 2000; Jacobsen et al., 2001a). Apparently, several mechanisms contribute to the sorption of atrazine. When the results in the upper soils were included, a positive correlation with the organic carbon content was observed by (Seybold et al., 1994) (the organic carbon fraction ranged from 0.05 to 0.65 in the experiments) suggesting hydrophobic partitioning to be of importance. However, other studies did not observe any correlation with the organic carbon content (Madsen et al., 2000; Roy and Krapac, 1994; Felding, 1997). The sorption mechanism studies using single minerals and iron oxides suggest van der Waals forces as a potential sorption mechanism (Clausen et al., 2001; Clausen and Fabricius, 2001). Several studies found a negative correlation with pH – especially in the lower pH range (Madsen et al., 2000; Rae et al., 1998; Roy and Krapac, 1994). At low pH values a larger fraction of atrazine becomes positively charged (pK$_a$-value of 1.7) and is thus attracted by electrostatic interactions to the negatively charged sites on the sediment.

**Degradation** of atrazine in aquifers has been extensively studied (Agertved et al., 1992; Widmer and Spalding, 1995; Johnson et al., 2000; Rügge et al., 1999a; Klint et al., 1993; Larsen et al., 2000; Arildskov et al., 2001; Papiernik, 2001; Pedersen, 2000; Mirgain et al., 1995; McMahon et al., 1992; Larsen and Aamand, 2001; Skark and Obermann, 1995; Levy and Chesters, 1995). Recalcitrance of this herbicide was observed in most experiment, aerobic as well as anaerobic. The exceptions were the study by (Mirgain et al., 1995) (using an extremely high initial concentration of 20 mg/L), the study by (Patterson et al., 2002) (only after addition of oxygen) (Figure 9), and a field study where indirect signs of very slowly degradation were observed (Levy and Chesters, 1995).
In contrast to the recalcitrance in aquifers, degradation of atrazine in topsoil has been demonstrated several times, likely due to the higher numbers of microorganisms in topsoil (Stolpe and Shea, 1995; Erickson and Lee, 1989; Cook, 1987; Shapir and Mandelbaum, 1997). The first step in the atrazine degradation process is the formation of either deethylatrazine, deisopropylatrazine or hydroxyatrazine. These metabolites are frequently found in groundwater.

3.3.5 BAM

The compound BAM is a metabolite from the herbicides chlortiamid and dichlobenil and constitutes the majority of the pesticide findings in Danish groundwater. The structural formula of BAM and some relevant physico-chemical characteristics are shown in Table 3.

**Sorption.** Only few studies have dealt with BAM sorption in sandy aquifers and all of them are Danish. The reported $K_d$-values range from approximately 0 to 0.1 L/kg corresponding to retardation factors of 1 to 1.6 (Tuxen et al., 2000; Broholm et al., I, 2001; Clausen et al., 2002) (Figure 10). Higher $K_d$-values, up to 0.93 L/kg, were observed in anaerobic clayey sediments (Clausen et al., 2002). In one study a correlation with clay content and organic carbon content was observed suggesting that hydrophobic partitioning with the organic carbon as well as van der Waals forces, might be the mechanisms involved (Clausen et al., 2002).
Degradation of BAM has not been proven in any of the investigations concerning BAM’s fate in aquifers (Tuxen et al., 2000; Tuxen et al., 2002; Broholm et al., 2001; Rügge et al., 2000; Pedersen, 2000; Clausen et al., 2002) (Figure 10). However, limited degradation of BAM was observed in some of the topsoils investigated (Clausen et al., 2002). The Pesticide Manual (Tomlin, 1997) states that BAM may be slowly degraded to 2,6-dichlorobenzamide.

3.3.6 Bentazone

Bentazone is a heterocyclic compound and not included in a general group of herbicides (Table 3). It is used for weed control in cereals, peas, and grass.

Sorption. In general, there was little bentazone sorption in the aquifers investigated: $K_d$-values ranged from 0 to 0.05 L/kg corresponding to retardation coefficients of approximately 1 to 1.3 (Tuxen et al., 2000; Broholm et al., 2001; Madsen et al., 2000) (Figure 10). Similar results were obtained in topsoil containing high amounts of organic carbon (Gaston et al., 1996; Huber and Otto, 1994). Likely, the almost complete dissociation of bentazone at the investigated pH values ($pK_a$ is 3.3) makes the compound very water soluble and consequently insusceptible to hydrophobic partitioning with the organic material. Sorption studies using single minerals found a small but significant sorption of bentazone at low pH-values – especially to iron oxides. It was suggested that the sorption mechanism was a weak electrostatic interaction between the anionic part of the molecule and the positive sites on the surfaces (Clausen et al., 2001; Clausen and Fabricius, 2001).

Degradation. Bentazone was recalcitrant in all the investigations using aquifer material (Broholm et al., 2001; Tuxen et al., 2000; Tuxen et al., 2002; Pedersen, 2000).
(Figure 10). In contrast, slow degradation has been observed in subsoils (van der Pas et al., 1998) and in aerobic soils (Huber and Otto, 1994; Wagner et al., 1996; Knauber et al., 2000). The degradation occurred as a microbial hydrolysis and some bentazone was completely mineralized whereas some was degraded to metabolites subsequently incorporated in humic materials (Wagner et al., 1996). No degradation was observed in topsoil under anaerobic conditions (Huber and Otto, 1994).

### 3.3.7 Overview

**Sorption of the selected herbicides.** The summarized results discussed here suggest that sorption of the 8 selected herbicides in aquifers is of minor importance. Retardation factors ranged from 1-3 for the phenoxy acids, BAM, and bentazone (Table 4). Sorption of DNOC, atrazine, and isoproturon was slightly higher under special conditions resulting in retardation factors up to 10. The special conditions include: high sorption of DNOC at low pH-values or in sediments with high content of specific clay minerals; high sorption of isoproturon in aquifers with high organic carbon content; and high sorption of atrazine at low pH-values or in sediments with high organic carbon content. The low retardation coefficients observed in aquifers imply that once the herbicides have leached into the groundwater, their mobility will be very high. Sorption in aquifers is thus not a crucial process when estimating potential travel times of herbicides from point sources. However, identification and understanding of sorption is of great importance in terms of interpreting data from experimental results.

### Table 4. Summary of sorption and degradation of the 8 selected herbicides in sandy aquifers (Agertved et al., 1992; Broholm et al., I, 2001; Madsen et al., 2000; Rügge et al., 1999a; Tuxen et al., 2000; Kristensen et al., 2001a; Broholm et al., II, 2001; Johnson et al., 1998; Seybold et al., 1994; Roy and Krapac, 1994; Widmer and Spalding, 1995; Xu et al., 1999; Jacobsen et al., 2001b; Clausen et al., 2002).

| Pesticide   | Sorption | Degradation | | | |
|-------------|----------|-------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
|             | K_d (L/kg) | R          | Aerobic | Anaerobic | Aerobic | Anaerobic | Aerobic | Anaerobic |
| Phenoxy acids | 0-0.26 | 1-2.5 | +/− | +/− | +/− | +/− | +/− | +/− |
| DNOC     | 0.1-0.98 | 1.5-6^b | +/− | +/− | +/− | +/− | +/− | +/− |
| Isoproturon | 0.03-0.85 | 1.2-6^d | +/− | +/− | +/− | +/− | +/− | +/− |
| Atrazine | 0-1.8 | 1-10^f | +/− | +/− | +/− | +/− | +/− | +/− |
| BAM      | 0-0.1 | 1-1.6 | +/− | +/− | +/− | +/− | +/− | +/− |
| Bentazone | 0-0.05 | 1-1.3 | +/− | +/− | +/− | +/− | +/− | +/− |

^a Includes MCPP, dichlorprop and 2,4-D; ^b The high sorption was observed in low pH aquifers; ^c Abiotic degradation; ^d The highest sorption was found in aquifers with f_{oc} > 0.05%; ^e Degradation only observed in chalk aquifers; ^f Sorption highest in aquifers with low pH and/or high f_{oc}; ^g Degradation was only observed in aquifer materials added oxygen.
Degradation of the selected herbicides. The reported degradability results for the 8 selected herbicides in aquifers are presented in Table 4. Most remarkable is the fact that all the herbicides showed recalcitrant behavior in some of the investigations. In contrast, some degree of degradation in topsoils has been reported for all herbicides. The most easily degradable compounds in aquifers were the phenoxy acids under aerobic conditions. Hence, biodegradation of herbicides in aquifers appears, from this literature review, to have the greatest potential with respect to phenoxy acids. However, a better understanding of the factors affecting the degradation of DNOC, isoproturon, and atrazine, as well as the practice of inoculating aquifers with the atrazine-degrading Pseudomonas sp. strains, could result in bioremediation of these compounds as well.
4. Physical and chemical remediation technologies

During the last 10 years many *in situ* remediation technologies have been developed in order to overcome the complicating issues that has been discovered at numerous sites. However, the experience regarding *in situ* remediation of pesticides in groundwater is scarce; probably due to the limited focus on this problem outside Europe. Due to the limited number of references, compounds similar in structure to the 8 selected herbicides are occasionally included in the following review. As well, *ex situ* technologies with potential of *in situ* implications are occasionally included.

4.1 Phase-transfer technologies

The physical remediation technologies are based on removal of either vapor, water or solid phase containing pesticides with subsequent treatment initiatives *ex situ*. Often, compounds will also be present in another phase than the one to be removed, implying transfer of the pesticides from one phase to another.

The most frequently-used remediation technology for xenobiotics in groundwater to date is pump and treat. However, a review of the success of this technology at 77 sites (not particularly pesticide sites) revealed that the clean-up goals were only met in 8 cases within a reasonable time frame (National Research Council, 1994). The conclusion of the review was, that in addition to problems associated with strongly sorbing compounds, heterogeneities in the geologic formations prevented restoration of aquifers. However, preliminary results from a site with complex geology and contaminated with metolachlor and dinoseb indicated that pump and treat could be successfully applied at the site (Carter et al., 1995) (Table 5).

**Table 5. Phase-transfer remediation technologies.**

<table>
<thead>
<tr>
<th>Technology</th>
<th>Type</th>
<th>Environ.</th>
<th>Compounds</th>
<th>Result</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pump and treat</td>
<td><em>In situ</em></td>
<td>Groundwater</td>
<td>Metolachlor, dinoseb</td>
<td>Successful (preliminary)</td>
<td>(Carter et al., 1995)</td>
</tr>
<tr>
<td>Activated carbon in funnel and gate</td>
<td><em>In situ</em></td>
<td>Groundwater</td>
<td>Many different</td>
<td>Successful (preliminary)</td>
<td>(Williamson et al., 2000)</td>
</tr>
<tr>
<td>Activated carbon</td>
<td>Lab.</td>
<td>Groundwater</td>
<td>Atrazine</td>
<td>Successful</td>
<td>(Knappe et al., 1997)</td>
</tr>
<tr>
<td>Organic sorbent</td>
<td><em>Ex situ</em></td>
<td>Wastewater</td>
<td>Many different</td>
<td>Successful</td>
<td>(Agdi et al., 2000)</td>
</tr>
</tbody>
</table>
The potential of using pump and treat as a remedial technology for the 8 selected herbicides is considered to be good, due to their relatively low sorption in aquifers with retardation coefficients less than 10 (National Research Council, 1994). The success will depend strongly on the hydrogeology at the sites and should be followed up by treatment actions of the extracted groundwater.

Remediation by enhanced sorption is the principle behind treatment of water in activated carbon filters on-site or ex situ. However, this technology can also be applied in situ using a funnel-and-gate system, with for instance, granular activated carbon as the reactive material in the gate. Such a system was implemented successfully at a former pesticide production site contaminated with DDT, toxaphene, atrazine, dieldrin, chlordane, lindane, alpha-BHC, endosulfan and methyl parathion (statement based on preliminary results) (Williamson et al., 2000) (Table 5). Potentially sorbents other than activated carbon, could be used, for example diatomaceous earth, as demonstrated ex situ using waste water contaminated with chlorpyriphos, methidathion, methyl parathion, atrazine and fenamiphos (Agdi et al., 2000). Due to the very high sorbing capacity of granular activated carbon, installations of funnel-and-gate systems with activated carbon as the reactive material in the gate, have the potential to be a remedial technology for the 8 herbicides. However, tests should be conducted in order to estimate the reactivity time of such a gate, which could be reduced due to sorption of other organic compounds in the groundwater (Knappe et al., 1997).

Thermal technologies (for example steam injection) can be disregarded as remediation technologies for the 8 selected herbicides. The high water solubilities of the selected herbicides and low vapor pressures make this technology unsuitable. Similarly, airsparging, which involves a mass transfer of contaminants from the water phase to the gas phase, would be unsuitable. However, the potential stimulating of biodegradation due to the addition of oxygen in airsparging should be assessed (see section 5.2).

4.2 Chemical transformation technologies

In contrast to physical remediation technologies, the goal of the chemical remediation technologies is to transform pesticides to less harmful products. Often, the chemical remediation technologies involve quite aggressive processes and aim to clean up the sites quickly and effectively. Chemical oxidation as well as chemical reduction of the pesticides has been suggested.

Several strong oxidants, such as ozone, hydrogen peroxide and potassium permanganate have been used for remediation of a number of xenobiotics (Wickramanayake et al., 2000). In some cases hydrogen peroxide is combined with an iron catalyst forming very reactive free radicals, the so-called Fenton’s reagent (Fenton, 1894).

The effect of ozone treatment on pesticides transformation have been studied in numerous laboratory experiments, but most investigations have focused on treatment of
wastewater (Chiron et al., 2000; Benoit-Goyod et al., 1986; Kearney et al., 1988; Reynolds et al., 1989; Somich et al., 1990; Hapeman-Somich et al., 1992; Beltrán et al., 1994; Hapeman et al., 1995; Speth, 1993; Adams and Randtke, 1992) (Table 6). In general, the success of the ozone treatment was dependent on the pesticide in question, although, a significant transformation occurred for most pesticides. A review by (Reynolds et al., 1989) revealed that particularly good results (evaluated by rapid and complete mineralization) were obtained for phenoxy acids and phenolic compounds. For most other pesticides ozonation resulted in formation of reaction products – often as toxic as the parent compound. However, post treatment by inoculation with specific microorganisms has been shown to be possible by several investigators (Kearney et al., 1988; Somich et al., 1990; Hapeman et al., 1995).

**Table 6. Chemical remediation technologies.**

<table>
<thead>
<tr>
<th>Techn.</th>
<th>Type</th>
<th>Environ.</th>
<th>Compounds</th>
<th>Result</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ozone</td>
<td>Lab.</td>
<td>Synthetic water</td>
<td>MCPA</td>
<td>Successful, but formation of degr. prod.</td>
<td>(Benoit-Goyod et al., 1986)</td>
</tr>
<tr>
<td>Ozone</td>
<td>Lab.</td>
<td>Waste-water</td>
<td>Atrazine</td>
<td>Successful, but formation of degr. prod. which were degraded by inoculated microorg.</td>
<td>(Kearney et al., 1988)</td>
</tr>
<tr>
<td>Ozone</td>
<td>Lab. + on site</td>
<td>Waste-water</td>
<td>Atrazine, cyanazine,</td>
<td>Successful</td>
<td>(Somich et al., 1990)</td>
</tr>
<tr>
<td>Ozone</td>
<td>Lab.</td>
<td>Waste-water</td>
<td>Atrazine</td>
<td>Successful, but formation of degr. prod.</td>
<td>(Adams and Randtke, 1992)</td>
</tr>
<tr>
<td>Ozone</td>
<td>Lab.</td>
<td>Synthetic water</td>
<td>MCPP</td>
<td>Successful</td>
<td>(Beltrán et al., 1994)</td>
</tr>
<tr>
<td>Ozone</td>
<td>Pilot scale</td>
<td>Waste-water</td>
<td>Atrazine</td>
<td>Successful, but formation of degr. prod. which were degraded by inoculated microorg.</td>
<td>(Hapeman et al., 1995)</td>
</tr>
<tr>
<td>Ozone</td>
<td>Lab.</td>
<td>Drinking water</td>
<td>Glyphosate</td>
<td>Successful</td>
<td>(Speth, 1993)</td>
</tr>
<tr>
<td>Ozone</td>
<td>Review</td>
<td>Water</td>
<td>Many different</td>
<td>Successful (best for phenoxy acids and phenolic compounds)</td>
<td>(Reynolds et al., 1989)</td>
</tr>
<tr>
<td>Ozone</td>
<td>Review</td>
<td>Waste-water</td>
<td>Many different</td>
<td>Successful, but formation of degr. prod.</td>
<td>(Chiron et al., 2000)</td>
</tr>
</tbody>
</table>

a Not a pesticide but similar in chemical structure to nitroaromatic pesticides (e.g. DNOC and dinoseb)
b Not a pesticide but similar in chemical structure to triazine pesticides (e.g. atrazine and simazine)
Table 6 continued.

<table>
<thead>
<tr>
<th>Techn.</th>
<th>Type</th>
<th>Environ.</th>
<th>Compounds</th>
<th>Result</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fenton</td>
<td>Lab.</td>
<td>Synthetic water</td>
<td>2,4-D and 2,4,5-T</td>
<td>Successful at low pH</td>
<td>(Pignatello, 1992)</td>
</tr>
<tr>
<td>Fenton</td>
<td>Lab.</td>
<td>Synthetic water</td>
<td>Atrazine</td>
<td>Successful at low pH, but formation of degr. prod.</td>
<td>(Arnold et al., 1995)</td>
</tr>
<tr>
<td>Fenton</td>
<td>Lab.</td>
<td>Wastewater and soil</td>
<td>TNT&lt;sup&gt;a&lt;/sup&gt;</td>
<td>Successful at low pH, but formation of degr. prod.</td>
<td>(Li et al., 1997a)</td>
</tr>
<tr>
<td>Fenton</td>
<td>Lab.</td>
<td>Synthetic water</td>
<td>Diuron</td>
<td>Successful</td>
<td>(Mazellier and Sulzberger, 2001)</td>
</tr>
<tr>
<td>Fenton</td>
<td>Lab.</td>
<td>Soil</td>
<td>TNT&lt;sup&gt;a&lt;/sup&gt;</td>
<td>Successful</td>
<td>(Li et al., 1997b)</td>
</tr>
<tr>
<td>Fenton</td>
<td>Lab.</td>
<td>Soil and water</td>
<td>RDX&lt;sup&gt;b&lt;/sup&gt;</td>
<td>Successful at high temp.</td>
<td>(Bier et al., 1999)</td>
</tr>
<tr>
<td>Fenton</td>
<td>Lab.</td>
<td>Wastewater</td>
<td>2,4-DCP</td>
<td>Successful</td>
<td>(Li et al., 1999)</td>
</tr>
<tr>
<td>Fenton</td>
<td>Lab.</td>
<td>Synthetic water</td>
<td>2,4-D</td>
<td>Successful</td>
<td>(Wang and Lemley, 2001)</td>
</tr>
<tr>
<td>Fenton</td>
<td>In situ</td>
<td>Soil</td>
<td>2,4-D</td>
<td>Successful</td>
<td>(Holish et al., 2000)</td>
</tr>
<tr>
<td>Fenton</td>
<td>Lab.</td>
<td>Soil and water</td>
<td>MNT&lt;sup&gt;a&lt;/sup&gt;, DNT&lt;sup&gt;b&lt;/sup&gt;, TNT&lt;sup&gt;a&lt;/sup&gt;</td>
<td>Successful</td>
<td>(Li et al., 1998)</td>
</tr>
<tr>
<td>Fenton</td>
<td>Lab.</td>
<td>Synthetic water</td>
<td>2,4-DCP</td>
<td>Successful at low pH</td>
<td>(Tang and Huang, 1996)</td>
</tr>
<tr>
<td>Fenton</td>
<td>Lab.</td>
<td>Wastewater</td>
<td>Atrazine, cyanazine, alachlor, metolachlor, EPTC</td>
<td>Successful</td>
<td>(Arnold et al., 1996)</td>
</tr>
<tr>
<td>Perman-</td>
<td>Lab.</td>
<td>Drinking water</td>
<td>Glyphosate</td>
<td>Not successful</td>
<td>(Speth, 1993)</td>
</tr>
<tr>
<td>ganate</td>
<td>Review</td>
<td>Groundwater</td>
<td>Many different</td>
<td>Successful</td>
<td>(Siegrist et al., 2001)</td>
</tr>
</tbody>
</table>

<sup>a</sup> Not a pesticide but similar in chemical structure to nitroaromatic pesticides (e.g. DNOC and dinoseb)<br>
<sup>b</sup> Not a pesticide but similar in chemical structure to triazine pesticides (e.g. atrazine and simazine)
A number of investigators have studied the potential of using Fenton’s reagent to remediate pesticide-contaminated wastewater and soil (Pignatello, 1992; Arnold et al., 1995; Arnold et al., 1996; Tang and Huang, 1996; Li et al., 1997a; Li et al., 1998; Li et al., 1997b; Bier et al., 1999; Li et al., 1999; Holish et al., 2000; Wang and Lemley, 2001; Mazellier and Sulzberger, 2001; Mazellier and Sulzberger, 2001) (Table 6). All the investigators found a rapid and complete mineralization of the compounds in question, with the exception of three studies where small amounts of degradation products were formed (Arnold et al., 1995; Li et al., 1997a; Arnold et al., 1996). In general, a significant effect on degradation rates was observed, with maximum rates obtained at very low pH (2-3). In many cases UV light, electrolysis or heat catalyzed the reaction.

Permanganate has been shown to be a viable oxidant in the removal of a number of chlorinated ethylenes and other recalcitrant compounds including phenols, nitroaromatic compounds, and triazines (Siegrist et al., 2001; Yan and Schwartz, 1999; Clayton et al., 2000). However, another investigation found that permanganate had less potential for removal of glyphosate from drinking water compared to other chemical oxidants (Speth, 1993). There are some limitations associated with using permanganate. Is is a weaker oxidant compared to ozone or Fenton’s reagent, and thus, permanganate may not be capable of oxidizing the most recalcitrant compounds. Additionally, precipitation of MnO \(_2\) and CO\(_2\) gas formation, which would reduce permeability in the matrix have the potential to limit in situ applications (Schroth et al., 2001). Permanganate does, however, have the advantage of being both more stable and persistent in subsurfaces than ozone or Fenton’s reagent, which facilitates mixing with the target pesticides.

In general, chemical oxidation of pesticides, can occur rapidly and effectively. However, the reagents are quite aggressive and often have a short lifetime, making it problematic to implement them in situ. Also, a poisonous gas like ozone can be difficult and dangerous to handle. Another problem is that these strong oxidants are non-specific, meaning that all other reduced compounds will be oxidized. In anaerobic aquifers or in aquifers with high organic carbon content, this will imply a very high consumption of expensive oxidants. Even worse, the treatment may have a significant effect on the surrounding environment; for example if pyrite oxidation occurs. Thus, the chemical oxidation of the 8 selected herbicides in situ, would be most feasible for treatment of source zones from large point sources (i.e. from chemical plants) in combination with other remediation technologies in the plume.

The use of zero-valent iron to reductively dehalogenate pesticides is a technology that has gained much attention over the last decade (Siantar et al., 1995; Agrawal and Tratnyek, 1996; Sayles et al., 1997; Hundal et al., 1997; Devlin et al., 1998; Eykholt and Davenport, 1998; Monson et al., 1998; Singh et al., 1998b; Singh et al., 1998a; Rajagopal and Burris, 1999; Singh et al., 1999; Ghauch et al., 1999; Ghauch and Suptil,
2000; Kim and Carraway, 2000; Ghauch et al., 2001; Ghauch, ; Klausen et al., 2001; Lavine et al., 2001; Dombek et al., 2001; Comfort et al., 2001; Oh et al., 2001) (Table 7). With the exception of one, all of these investigations were laboratory investigations, and a number of different pesticides were tested. Most authors concluded that zero-valent iron was successful in transforming the target compound at high rates. However, most reports on nitroaromatic compounds (Agrawal and Tratnyek, 1996; Klausen et al., 2001; Lavine et al., 2001) and phenolic compounds (Kim and Carraway, 2000) observed limited reduction due to hydroxides precipitating on the iron surface. In all the experiments, accumulation of the dehalogenated compounds was observed, many of which were as toxic as the parent compounds. The rate of dehalogenation was found to be extremely dependent on the groundwater composition, in particular pH, redox conditions, and inorganic compounds.

Table 7. Zero valent iron remediation technologies.

<table>
<thead>
<tr>
<th>Techn.</th>
<th>Type</th>
<th>Environ.</th>
<th>Compounds</th>
<th>Result</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe⁰</td>
<td>Lab.</td>
<td>Ground-water</td>
<td>DBCP</td>
<td>Successful (not at high O₂-conc.)</td>
<td>(Siantar et al., 1995)</td>
</tr>
<tr>
<td>Fe⁰</td>
<td>Lab.</td>
<td>Synthetic water</td>
<td>Nitroaromatic compoundsᵃ</td>
<td>Successful, but prod. of degr. prod.</td>
<td>(Agrawal and Tratnyek, 1996)</td>
</tr>
<tr>
<td>Fe⁰</td>
<td>Lab.</td>
<td>Synthetic water</td>
<td>DDT, DDD, DDE</td>
<td>Successful, but prod. of degr. prod.</td>
<td>(Sayles et al., 1997)</td>
</tr>
<tr>
<td>Fe⁰</td>
<td>Lab.</td>
<td>Synthetic water and soil</td>
<td>TNTᵃ, RDXᵇ</td>
<td>Successful, but formation of degr. prod. which were degraded by inoculated microorg.</td>
<td>(Hundal et al., 1997)</td>
</tr>
<tr>
<td>Fe⁰</td>
<td>Lab.</td>
<td>Synthetic water</td>
<td>Nitroaromatic compoundsᵃ</td>
<td>Successful, but prod. of degr. prod.</td>
<td>(Devlin et al., 1998)</td>
</tr>
<tr>
<td>Fe⁰</td>
<td>Lab.</td>
<td>Synthetic water</td>
<td>Alachlor, metolachlor</td>
<td>Successful, but prod. of degr. prod.</td>
<td>(Eykholt and Davenport, 1998)</td>
</tr>
<tr>
<td>Fe⁰</td>
<td>Lab.</td>
<td>Synthetic water</td>
<td>Atrazine</td>
<td>Successful, but prod. of degr. prod.</td>
<td>(Monson et al., 1998)</td>
</tr>
<tr>
<td>Fe⁰</td>
<td>Lab.</td>
<td>Water and soil</td>
<td>Atrazine</td>
<td>Successful, but prod. of degr. prod.</td>
<td>(Singh et al., 1998b)</td>
</tr>
</tbody>
</table>

ᵃ Not a pesticide but similar in chemical structure to nitroaromatic pesticides (e.g. DNOC and dinoseb)  
b Not a pesticide but similar in chemical structure to triazine pesticides (e.g. atrazine and simazine)
<table>
<thead>
<tr>
<th>Techn. Type</th>
<th>Type</th>
<th>Environ.</th>
<th>Compounds</th>
<th>Result</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe&lt;sup&gt;0&lt;/sup&gt;</td>
<td>Lab.</td>
<td>Water and soil</td>
<td>RDX&lt;sup&gt;b&lt;/sup&gt;</td>
<td>Successful, but prod. of degr. prod.</td>
<td>(Singh et al., 1998a)</td>
</tr>
<tr>
<td>Fe&lt;sup&gt;0&lt;/sup&gt;</td>
<td>Lab.</td>
<td>Synthetic water</td>
<td>1,2-dibromoethane</td>
<td>Successful</td>
<td>(Rajagopal and Burris, 1999)</td>
</tr>
<tr>
<td>Fe&lt;sup&gt;0&lt;/sup&gt;</td>
<td>Lab.</td>
<td>Wastewater</td>
<td>Atrazine, parathion</td>
<td>Successful, but prod. of degr. prod.</td>
<td>(Ghauch et al., 1999)</td>
</tr>
<tr>
<td>Fe&lt;sup&gt;0&lt;/sup&gt;</td>
<td>Lab.</td>
<td>Synthetic water</td>
<td>Atrazine, propazine, simazine</td>
<td>Successful, but prod. of degr. prod.</td>
<td>(Ghauch and Suptil, 2000)</td>
</tr>
<tr>
<td>Fe&lt;sup&gt;0&lt;/sup&gt;</td>
<td>Lab.</td>
<td>Synthetic water</td>
<td>Carbaryl</td>
<td>Successful, but prod. of degr. prod.</td>
<td>(Ghauch et al., 2001)</td>
</tr>
<tr>
<td>Fe&lt;sup&gt;0&lt;/sup&gt;</td>
<td>Lab.</td>
<td>Synthetic water</td>
<td>Benomyl, picloram, dicamba</td>
<td>Successful, but prod. of degr. prod.</td>
<td>(Ghauch, 2001)</td>
</tr>
<tr>
<td>Fe&lt;sup&gt;0&lt;/sup&gt;</td>
<td>Lab.</td>
<td>Synthetic water</td>
<td>Nitroaromatic compounds&lt;sup&gt;a&lt;/sup&gt;</td>
<td>Not successful</td>
<td>(Klausen et al., 2001)</td>
</tr>
<tr>
<td>Fe&lt;sup&gt;0&lt;/sup&gt;</td>
<td>Lab.</td>
<td>Synthetic water</td>
<td>Nitroaromatic compounds&lt;sup&gt;a&lt;/sup&gt;</td>
<td>Not successful</td>
<td>(Lavine et al., 2001)</td>
</tr>
<tr>
<td>Fe&lt;sup&gt;0&lt;/sup&gt;</td>
<td>Lab.</td>
<td>Synthetic water</td>
<td>Atrazine</td>
<td>Successful at low pH, but prod. of degr. prod.</td>
<td>(Dombek et al., 2001)</td>
</tr>
<tr>
<td>Fe&lt;sup&gt;0&lt;/sup&gt;</td>
<td>In situ</td>
<td>Soil, sludge, ground-water</td>
<td>RDX&lt;sup&gt;b&lt;/sup&gt;</td>
<td>Successful, but formation of degr. prod. which were degraded by inoculated microorg.</td>
<td>(Comfort et al., 2001)</td>
</tr>
<tr>
<td>Fe&lt;sup&gt;0&lt;/sup&gt;</td>
<td>Lab.</td>
<td>Soil</td>
<td>Metolachlor</td>
<td>Successful, but prod. of degr. prod.</td>
<td>(Oh et al., 2001)</td>
</tr>
</tbody>
</table>

<sup>a</sup> Not a pesticide but similar in chemical structure to nitroaromatic pesticides (e.g. DNOC and dinoseb)

<sup>b</sup> Not a pesticide but similar in chemical structure to triazine pesticides (e.g. atrazine and simazine)

The implementation of chemical reduction of pesticides by zero-valent iron involves the installation of a funnel-and-gate system, where zero-valent iron is the reactive material in the gate. To date, numerous pilot-scale and full-scale installations for remediation of chlorinated solvents have been discussed in the scientific literature (RTDF, 2000). However, potential long-term problems such as precipitation of hydroxides which
would cover the active surfaces and decrease permeability of the wall, redox limitations, and bioclogging have not been extensively assessed. Chemical reduction of herbicides using zero-valent-iron has been proven for atrazine, and is also believed to have potential for the other halogenated herbicides (phenoxy acids, DNOO and BAM). Subsequent treatment may, however, be necessary to remove recalcitrant and/or toxic degradation products.
5. Bioremediation technologies

The goal of bioremediation of pesticides in groundwater is to transform the compounds completely to \( \text{CO}_2 \), \( \text{H}_2\text{O} \), and inorganic salts via biological processes. Bioremediation takes advantages of natural processes and is thus attractive from an ecological point of view. It is often also relatively inexpensive compared to other technologies. In this thesis two bioremediation technologies, natural attenuation (NA) and biostimulation will be emphasized.

5.1 Natural attenuation

The principle of NA is that naturally occurring processes in the subsurface reduce mass of critical contaminants to avoid risk to downgradient receptors. The processes involved are dilution, dispersion, sorption, volatilization, and degradation. A crucial point in the assessment of NA is whether the specific herbicides in question are degraded. Based on the observed degradation of phenoxy acids in aerobic aquifers in most cases (see section 3.3.1), NA might be an applicable remediation solution for such herbicides.

In order to obtain sufficient degradation rates for the phenoxy acids, a microbial population capable of degrading the compounds must develop. At many phenoxy acid point source sites, the concentrations are so low (in the \( \mu\text{g/L} \) range, see section 2), that growth of specific microorganisms may not be supported (Alexander, 1999). As part of a natural gradient field injection experiment a section of the Vejen aquifer was continuously exposed to low phenoxy acid concentrations (approximately 40 \( \mu\text{g/L} \)) for seven months. After an initial lag phase of 80-100 days, rapid degradation of MCPP and dichlorprop was observed (see Figure 5 section 3.3.1). The phenoxy acid concentrations decreased to below the detection limit within the first meter downgradient from the injection wells, corresponding to a hydraulic retention time in the aquifer of less than 3 days (Broholm et al., I, 2001). These observations indicate that the microbial community acclimated to the herbicides.

Subsequent laboratory experiments with aquifer material exposed to different masses of phenoxy acids in the field injection experiment were conducted, in order to elucidate the observed acclimation (de Lipthay et al., IV, 2002; Tuxen et al., III, 2002). Correlations were found between the field exposure to the phenoxy acids and the amount degraded after 50 days of incubation in the laboratory, and between field exposure to the phenoxy acids and the number of specific phenoxy acid degrading bacteria in the sediment (Figure 11) (Tuxen et al., III, 2002). Furthermore, the presence of \( tfd \)-genes know to be present among phenoxy acid degraders, were only found in the exposed part of the aquifer (de Lipthay et al., IV, 2002). Modeling of the degradation of the phenoxy acids in the field injection experiment (Højberg, 2001) and in the laboratory experiments (Tuxen et al., III, 2002) was only successful using a growth based degradation kinetic.
Combined, these observations strongly suggest that injection of the phenoxy acids lead to a proliferation of specific degrading microorganisms carrying tfd-genes, which resulted in a high degradation potential in the aquifer after the initial lag phase. It was also observed that these microorganisms were capable of degrading the similar phenoxy acid 2,4-D, and that most of the degraded phenoxy acids were completely mineralized (Tuxen et al., III, 2002).

The observed proliferation of specific phenoxy acid degrading bacteria due to exposure to the compounds supports the use of NA as a remedial treatment at phenoxy acid point source sites. After the initial growth period, the degradation will likely be rapid enough to fulfill the regulatory requirements. Some phenoxy acid mass though, will escape from the source during the growth phase. The advanced numerical model which was developed to quantify the degradation in the field injection experiment, was set up in a two-dimensional version, to evaluate the long-term fate of this escaped mass (Figure 12) (Tuxen et al., V, 2002). In the scenario depicted in Figure 12, which was based on the hydraulic characteristics of the Vejen aquifer and the estimated and measured degradation parameters, the mass that escaped during the growth phase, was small compared to the injected mass. This mass however, was only slowly degraded and continued to travel with the flowing groundwater. Understanding of the dynamics of
plume development is crucial when assessing NA as a remediation technology at a site, and the simulations showed that even though a high degradation potential is observed close to the source, contamination could still exist further downgradient from the source. Of course, the significance of this process will be strongly dependent on the actual combination of source concentration, transport and microbial processes.

Figure 12. Snapshots at days 50, 600, and 2000 from a simulated release of phenoxy acids into a homogeneous aquifer. The inlet concentration was 25 µg/L and the contour lines (from outwards and inwards) correspond to concentrations of 0.1, 0.25, 0.5, 1.0, and 10.0 µg/L. From (Tuxen et al., V, 2002).

Natural attenuation was assessed as a remediation technology at an old landfill site contaminated with phenoxy acids (Tuxen et al., VI, 2002) (Table 8). Mass removal of the phenoxy acids within 50-100 m from the landfill was shown by calculations of contaminant fluxes passing monitoring fences at three distances. There was agreement between increasing oxygen concentrations with distance from the landfill and decreasing phenoxy acid concentrations indicating that aerobic degradation was a major removal process. Further evidence of degradation was the presence of putative phenoxy acid metabolites. In addition, phenoxy acids in the aquifer material were observed to degrade under controlled laboratory conditions. These evidences all indicate that natural attenuation may be a viable remediation solution at the site.

Several problems however, were encountered with respect to identifying definitive degradation indicators which could be used in the assessment. Dilution and flux calculations were difficult, due to the lack of a significant tracer and the non-stationarity of the source. Depletion of electron acceptors close to the source could not be attributed
to degradation of the phenoxy acids present in µg/L concentrations, but rather to the degradation of other organic compounds present in mg/L concentrations in the plume. Using the presence of putative phenoxy acid metabolites as evidence of ongoing degradation was interfered by the potential presence of these metabolites as impurities in the original pesticide product. Evaluation of other assessment tools such as changes in enatiomeric ratios of the chiral compounds, changes in compound-specific stable carbon isotope ratios, or occurrences of specific degraders or genes should be undertaken in future studies.

Remediation via natural attenuation of phenoxy acids has been assessed for an aquifer underlying a manufacturing site previously used for herbicide production (Klecka et al., 2001) (Table 8). The aquifer was aerobic and the primary pollutants were 2,4-D and 2,4,5-T. Concentrations of the phenoxy acids were variable in time and space with a maximum total concentration of 7,200 µg/L. Laboratory experiments using aquifer material from the site indicated that aerobic degradation was occurring in the aquifer, and microbial measurements indicated that the indigenous microorganisms were capable of degrading the phenoxy acids in question. It was concluded that natural attenuation occurred at the site.

The natural attenuation of the phenoxy acid MCPP was investigated in the anaerobic part of an aquifer downgradient from an old landfill (Baun et al., 2002) (Table 8). Although concentrations decreased from 600 µg/L to 30 µg/L 150 m downgradient from the landfill, this was shown to be governed by dilution alone and not degradation. These results are in agreement with numerous studies showing recalcitrance of MCPP under anaerobic conditions (section 3.3.1). A previous study observed the disappearance of MCPP at larger distances from the landfill where the conditions were aerobic (Lyngkilde and Christensen, 1992).

In summary, the results suggest that NA may be a viable remediation method for phenoxy acids under aerobic conditions but not under anaerobic conditions (Klecka et al., 2001; Baun et al., 2002; Tuxen et al., VI, 2002). The occasional observations regarding degradation of DNOC and the observed degradation of isoproturon in aerobic chalk aquifers, suggest that these compounds may also be remediated in some aquifers. However, natural attenuation of BAM and bentazone seems limited, due to their recalcitrant behaviour in all the investigations and cited experiments.
### Table 8. Bioremediation technologies.

<table>
<thead>
<tr>
<th>Techn.</th>
<th>Type</th>
<th>Environ.</th>
<th>Compounds</th>
<th>Result</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>NA</td>
<td><em>In situ</em></td>
<td>Groundwater</td>
<td>2,4-D, 2,4,5-T</td>
<td>Successful</td>
<td>(Klecka et al., 2001)</td>
</tr>
<tr>
<td>NA</td>
<td><em>In situ</em></td>
<td>Groundwater</td>
<td>Phenoxy acids</td>
<td>Successful</td>
<td>(Tuxen et al., VI, 2002)</td>
</tr>
<tr>
<td>NA</td>
<td><em>In situ</em></td>
<td>Groundwater</td>
<td>MCPP</td>
<td>Not successful</td>
<td>(Baun et al., 2002)</td>
</tr>
<tr>
<td>Biostim.</td>
<td>Lab.</td>
<td>Groundwater</td>
<td>MCPP</td>
<td>Successful</td>
<td>(Tuxen et al., VII, 2002)</td>
</tr>
<tr>
<td>Biostim.</td>
<td>Lab.</td>
<td>Groundwater</td>
<td>Atrazine</td>
<td>Successful</td>
<td>(Patterson et al., 2002)</td>
</tr>
<tr>
<td>Biostim.</td>
<td>Lab.</td>
<td>Groundwater</td>
<td>Fenamiphos,</td>
<td>Not successful</td>
<td>(Patterson et al., 2002)</td>
</tr>
<tr>
<td>Bioaug.</td>
<td>Lab.</td>
<td>Soil</td>
<td>Dinoseb</td>
<td>Successful</td>
<td>(Kaake et al., 1992)</td>
</tr>
<tr>
<td>Bioaug.</td>
<td>Lab.</td>
<td>Groundwater</td>
<td>Atrazine</td>
<td>Successful</td>
<td>(Shapir et al., 1998)</td>
</tr>
<tr>
<td>Bioaug.</td>
<td>Lab.</td>
<td>Groundwater</td>
<td>Atrazine</td>
<td>Successful</td>
<td>(Franzmann et al., 2000)</td>
</tr>
<tr>
<td>Bioaug.</td>
<td>Lab.</td>
<td>Groundwater</td>
<td>Atrazine</td>
<td>Successful</td>
<td>(Kristensen et al., 2001a)</td>
</tr>
<tr>
<td>Phyto.</td>
<td>Review of in situ</td>
<td>Groundwater</td>
<td>Many different</td>
<td>Not reported</td>
<td>(US EPA, 2000)</td>
</tr>
<tr>
<td>Phyto.</td>
<td>Lab.</td>
<td>Soil + synt. water</td>
<td>Atrazine</td>
<td>Successful</td>
<td>(Burken and Schnoor, 1996)</td>
</tr>
<tr>
<td>Phyto.</td>
<td>Lab.</td>
<td>Soil</td>
<td>Atrazine</td>
<td>Successful, but formation of degr. prod</td>
<td>(Burken and Schnoor, 1997)</td>
</tr>
<tr>
<td>Phyto.</td>
<td>Lab.</td>
<td>Soil</td>
<td>Aldrin, dieldrin</td>
<td>Not successful</td>
<td>(Williams et al., 2000)</td>
</tr>
</tbody>
</table>

*a* Not a pesticide but similar in chemical structure to nitroaromatic pesticides (e.g. DNOC and dinoseb)

*b* Not a pesticide but similar in chemical structure to triazine pesticides (e.g. atrazine and simazine
5.2. Biostimulation

Biostimulation is the technology where an optimal environment to enhance the intrinsic biodegradative potential of the indigenous microorganisms is created. Creation of an optimal environment may involve injections of nutrients, a primary carbon source, or changes of redox conditions by injecting oxygen or oxygen consuming compounds, if anaerobic conditions are preferable. Biostimulation of pesticides in soils has been investigated quite thoroughly (for review see (Zablotowicz et al., 1998)). Investigations of biostimulation of pesticides in aquifers are scarce and have only dealt with addition of oxygen (Table 8).

As discussed previously phenoxy acids are often observed to be recalcitrant under anaerobic conditions. At many point source sites anaerobic conditions prevail due to leaching of high concentrations of oxygen-consuming compounds such as organic carbon or ammonium. Stimulation of biodegradation by addition of oxygen to anaerobic aquifers has been feasible for organic compounds such as MTBE (Salanitro et al., 2000; Wilson et al., 2002) and BTEX compounds (Borden et al., 1997; Chapman et al., 1997). Laboratory experiments with aquifer material from two anaerobic phenoxy acid point sources were conducted to test the viability of this technology for phenoxy acids (Tuxen et al., 2002). The addition of oxygen significantly increased the microbial degradation. The effect of various oxygen concentrations was seen at several parameters: increasing the oxygen concentrations from less than 0.3 mg/L up to 7-8 mg/L shortened the lag phases (from up to 150 days to 5-25 days), and increased 1. order degradation rate constants (from approximately $5 \cdot 10^{-2}$ days$^{-1}$ to up to $30 \cdot 10^{-2}$ days$^{-1}$). Additionally, an increase in the degree of mineralization of MCPP was observed (30-50 % mineralized at low oxygen concentrations and 50-70 % mineralized at high oxygen concentrations, based on CO$_2$ recovery) (Figure 13). Thus, biostimulation by means of adding oxygen to phenoxy acids seems promising from a microbial point of view.

Several issues should be assessed before the technology is to be implemented. The injected oxygen is likely to react with compounds other than the phenoxy acids in anaerobic aquifers. Oxidation of Fe$^{2+}$ and Mn$^{2+}$ was observed in the investigated aquifers. Oxygen consumption was limited though, due to the relatively low initial concentrations of these compounds. In other, more anaerobic aquifers, oxidation of reduced iron and manganese, especially in the sediment phase, may be major oxygen consuming processes. The laboratory results indicated, however, that positive effects on biodegradation were obtained at oxygen concentrations down to 2 mg/L. Other oxygen consumers in addition to reduced iron and manganese have been observed at some sites. At one of the investigated sites, leaching from an old manure tank resulted in elevated concentrations of ammonium and non-volatile organic carbon (NVOC). Addition of
oxygen to these aquifer materials resulted in oxidation of a large part of the NVOC and of the ammonium. In two aquifer materials, however, ammonium oxidation (nitrification) was not observed, possibly due to toxic effects of the very high concentrations of phenoxy acids and chlorinated phenols on the nitrifying bacteria (up to 1000 µg/L).

Figure 13. Effects on oxygen concentration on MCPP degradation parameters. A: Length of lag phases, B: 1. order degradation rate constants, and C: Final evolved $^{14}CO_2$, as functions of oxygen concentrations. From (Tuxen et al., VII, 2002).

Other practical problems relate to the injection of oxygen in the aquifers and to providing sufficient mixing between the oxygen and phenoxy acids. The laboratory results discussed here were obtained in frequently shaken microcosms optimizing the mixing. However, especially in heterogeneous aquifers, there is a risk that the injected oxygen will travel via highly permeable zones in the aquifer, while a fraction of the contamination may be located in the low permeable zones of the aquifer. Because addition of oxygen is found to stimulate biodegradation of several compounds, much research is dedicated to this issue internationally. Likely, advances made in this research
will make biostimulation by addition of oxygen in anaerobic aquifers a viable remedial technology for phenoxy acids.

The effect on oxygen addition on biodegradation of atrazine has been investigated. A column experiment was conducted using aquifer material from an atrazine point source site and oxygen was delivered using a polymer mat (Patterson et al., 2002) (Table 8). A significant increase in degradation of atrazine was observed (Patterson et al., 2002), whereas additional supplements of acetate had no further effect (Figure 9, section 3.3.4). Oxygen addition had no effect on biodegradation of the pesticides fenamiphos and terbutryn (Patterson et al., 2002) (Table 8).

Although the number of references is limited, experimental results presented in this thesis and in the literature suggest that biostimulation in terms of oxygen addition could potentially be applied at phenoxy acid and atrazine point source sites. The occasional observed degradation of DNOC and the observed degradation of isoproturon in aerobic chalk aquifers, suggest that these compounds could also be remediated by biostimulation, if the parameters controlling the degradation can be identified. The potential of bioremediation seems very limited though, with respect to BAM and bentazone.

5.3 Other bioremediation technologies

Bioaugmentation is the technology where aquifers are inoculated with specific degrading microorganisms, often accompanied with biostimulation of these specific degraders. A *Pseudomonas* sp. strain, ADP, which harbors the genes for rapid and complete mineralization of atrazine has been isolated and characterized (Mandelbaum et al., 1995). Inoculation of aquifer material with this microorganism has been shown in laboratory experiments to increase mineralization of atrazine (Shapir et al., 1998; Franzmann et al., 2000; Kristensen et al., 2001a) (Table 8). One study showed that the positive effect was increased when oxygen was added as well (Franzmann et al., 2000). No literature could be found regarding the use of bioaugmentation in aquifers for pesticides other than atrazine, but the technology has been proven successful for treatment of the pesticide dinoseb in soil (Kaake et al., 1992) (Table 8).

The biggest challenge in applying bioaugmentation to a field site is to get the injected microcosms to survive the competition with other microorganisms. This issue requires an in-depth understanding of the conditions which favor the microorganisms in question. Remediation of atrazine contaminated groundwater using bioaugmentation appears promising, and this technology may also be suitable for the other selected herbicides (with the exception of BAM) for which specific degraders have been identified.

Phytoremediation uses plants to remediate contaminants either via direct uptake in the plant material and subsequent transformation in the plant, or via enhancement of
mineralization in the rhizosphere. The US EPA lists 14 phytoremediation pesticide projects, whereof 9 projects involve remediation of groundwater (US EPA, 2000) (Table 8). Since phytoremediation projects last for several decades, the success of these projects has not been evaluated. Phytoremediation of atrazine has been shown to enhance removal from soil (Burken and Schnoor, 1996; Burken and Schnoor, 1997). In contrast, a pilot-scale investigation with phytoremediation of the pesticides aldrin and dieldrin in soil, had no effect on the concentrations – probably because they are contact insecticides, which are not taken up and not translocated in significant amounts (Williams et al., 2000).

All systemic herbicides (this includes 2,4-D, bentazone, MCPP and other weak acids) are taken up and are translocated by plants, and are therefore potential candidates for phytoremediation. However, the phytotoxicity (which is another common property of herbicides) restricts the potential to non-target plants, or to concentrations below the toxic level for the selected plant. Uptake of weakly acidic herbicides is only efficient in acidic soils and aquifers (pH < 6.5), due to the "ion trap effect" (Bromilow and Chamberlain, 1995). Due to physiological reasons, plant roots can rarely grow deeper than 1 to 3 meters. Therefore, only shallow aquifers can be treated using phytoremediation. However, plants can be used to influence the water balance at a site, and to prevent pesticide transport off site (Trapp and Karlson, 2001).
6. Conclusions and perspectives

Herbicides in groundwater pose a great threat to the drinking water supplies in Denmark and other countries. A significant part of this contamination arises from point sources, for example machine pools, old landfills or accidental spills during handling.

Sorption of 8 selected herbicides: MCPP, dichlorprop, 2,4-D, DNOC, isoproturon, atrazine, BAM and bentazone was found to be of minor importance in aquifers, primarily due to the low organic carbon content in aquifers. All the herbicides were found to be recalcitrant under certain aquifer conditions. However, with few exceptions, the phenoxy acids were readily degradable under aerobic conditions. Also DNOC, isoproturon, and atrazine can be degraded in some aquifers. No literature reporting degradation of BAM and bentazone in aquifers was found. Although the 8 selected herbicides are among the most frequently found pesticides in groundwater, knowledge of the fate of the numerous other pesticide contaminants is required in order to assess potential remediation technologies.

Little research has been conducted regarding in situ remediation technologies for herbicides. In contrast, several technologies have been developed for ex situ treatment of herbicides; mainly with the focus on treatment of wastewater from pesticide formulation plants. However, based on the knowledge of the processes governing the fate of the herbicides in groundwater and the success rate of the ex situ technologies, assessment of the viability of the various in situ technologies was made (Table 9).

Laboratory and field experiments showed that the selected phenoxy acids (MCPP, dichlorprop, and 2,4-D) could be degraded in aerobic aquifers after lag phases. The lag phases are probably growth periods where specific microorganisms proliferate due to the exposure to the phenoxy acids – even at μg/L concentrations. These results combined with a successful application of natural attenuation at an aerobic phenoxy acid point source site, demonstrate the high potential for applying natural attenuation as a remediation technology for phenoxy acids under aerobic conditions. However, natural attenuation is not considered to be a viable remedy of phenoxy acids under anaerobic conditions, due to their recalcitrance in such redox environments.

In anaerobic aquifers stimulation of biodegradation of phenoxy acids by addition of oxygen was shown to be feasible from a microbial point of view. Even at low oxygen concentrations (2 mg/L) lag phases were shortened and degradation rates were increased in laboratory experiments. Oxidation of other organic carbon compounds and ammonium occurred in the microcosms indicating that effects associated with the addition of oxygen may complicate in situ applications.

In general, the experiments conducted and the literature reviewed suggest that a number of different in situ technologies exist, which could be feasible to remediate groundwater contaminated by herbicides from point sources. However, the number of potential point
sources is very high and it is therefore not possible to remediate them all from an economic point of view. More knowledge is required regarding risk assessments of the different types of point sources in order to focus future remediation initiatives.

**Table 9. Summarized evaluation of using the reviewed technologies for remediation of the 8 selected herbicides in aquifers.**

<table>
<thead>
<tr>
<th>Remediation technology</th>
<th>Evaluation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pump and treat</td>
<td>Could theoretically be successful in homogeneous aquifers due to the herbicides high water solubilities and the experimentally determined low retardation factors. Require subsequent treatment. Has been successfully implemented.</td>
</tr>
<tr>
<td>Enhanced sorption</td>
<td>Due to the very high sorbing capacity of granular activated carbon, installations of funnel-and-gate systems with activated carbon as the reactive material in the gate, could be successful. Long term in situ applications are needed to assess the reactive lifetime of such gates.</td>
</tr>
<tr>
<td>Thermal techn. and airsparging</td>
<td>Theoretically limited potential due to the high water solubilities and low vapor pressures of the herbicides.</td>
</tr>
<tr>
<td>Chemical oxidation</td>
<td>Laboratory experiments suggest a high potential, but formation of recalcitrant and toxic degradation products require additional treatment. In situ application involves a number of engineering problems.</td>
</tr>
<tr>
<td>Zero valent iron</td>
<td>Laboratory experiments suggest a high potential, but formation of recalcitrant and toxic degradation products require additional treatment.</td>
</tr>
<tr>
<td>Natural attenuation</td>
<td>Has been implemented successfully for phenoxy acids in aerobic aquifers, but is not viable for phenoxy acids in anaerobic aquifers. May theoretically also be viable for DNOC and isoproturon in some cases.</td>
</tr>
<tr>
<td>Biostimulation</td>
<td>Laboratory experiments suggest a potential for phenoxy acids and atrazine. May theoretically also be viable for DNOC and isoproturon in some cases.</td>
</tr>
<tr>
<td>Bioaugmentation</td>
<td>Laboratory experiments suggest a potential for atrazine. May theoretically also be viable for the other herbicides (except BAM) for which specific degraders have been isolated.</td>
</tr>
<tr>
<td>Phytoremediation</td>
<td>Theoretically potential at concentrations below the toxic level for the selected plant. Only relevant for shallow aquifers.</td>
</tr>
</tbody>
</table>
7. References


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