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LITERATURE STUDY ON REDOX CONTROL FOR INFILTRATION PONDS AND OTHER SUBSURFACE SYSTEMS

Project acronym: OXIRED-2

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Title

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Abstract

Artificial Recharge (AR) is a method to replenish groundwater in case of insufficient water availability or poor quality. For drinking water production, AR is often used as water purification step to avoid direct surface water abstraction. Besides physical filtration, purification is achieved through chemical processes like precipitation, sorption and (bio-) degradation. These are usually closely linked to redox conditions. It is the activity of micro-organisms and related chemical reactions that change the redox conditions, which in turn control the presence of substances and therefore the water quality. Typical pollutants in surface water that need to be addressed are organic compounds (e.g. pharmaceutical residues or pesticides), pathogens and heavy metals.

The purpose of this report is to introduce the theoretical background on redox zoning in infiltration ponds and to review publications in the search for applicable methods capable of controlling redox conditions. This shall serve as basis for further laboratory and technical scale experiments in the course of the OXIRED project.

The “optimal redox zonation” for maximum removal of redox-dependent substances is a concept with the aim of defining optimum residence times based on the degradation kinetics of contaminants in the source water: If substances or substance groups that show enhanced removal under anoxic to anaerobic conditions are not present in the source water at drinking water relevant concentrations, anoxic to anaerobic conditions should be avoided in order not to mobilize iron and other inorganic trace elements. Maximum benefit for aerobic subsurface passage is reached after 30 d, for anoxic / anaerobic subsurface passage after 100 d. However, already 15 d of aerobic and 2 d of anoxic / anaerobic passage lead to substantial removal or redox-sensitive substances or substance groups.

The main drivers for redox zonation in AR systems are the availability of oxidizing agents (oxygen, nitrate), of reducing agents (organic matter, reduced mineral phases), of nutrients, the biological activity (in infiltration pond and subsurface), and the residence time. These drivers are in turn controlled by many natural, site-specific (exogenous) and design & operation-related (decision) variables. Exogenous variables are e.g. aquifer geochemistry, temperature or natural groundwater recharge whereas the decision variables comprise factors such as pond geometry, distance between pond and well, well depth, pumping rate etc.

Theoretically, a wide range of possibilities could be applied to adjust the infiltration pond, the hyporheic zone and the subsurface passage, but only few seem technically feasible. These are e.g. the control of sunlight and temperature in the infiltration pond and upper sediment, the control of water movement in the pond to avoid excessive algal growth while enriching the water with oxygen. For the same reason nutrients could be added or avoided, influencing biomass production. Specific filter material could be used with defined content and characteristic of organic carbon to serve as electron acceptors. Infiltration rates could be controlled by adjusting the hydraulic head in order to enhance the formation of an unsaturated zone. Further downstream the application of redox controlling substances via injection wells could be possible, as well as controlling the residence times by adjusting pumping rates or creating hydraulic barrier wells at different distances from infiltration pond. For newly constructed AR systems the well field design (pond geometry, distance between pond and well, well depth) could be optimized with respect to redox zonation, as long as the other requirements (mainly sufficient production rates) are met.

No examples for redox control in infiltration ponds were identified. Therefore, two examples of redox control measures are described: the first serves an artificial re-oxidation of a polluted aquifer “BIOXWAND®” and the second provides injection of treated water to influence the redox conditions in the aquifer “Vyridox” and “Nitridox”.

Résumé

La recharge artificielle est une méthode utilisée pour réalimenter les nappes souterraines lorsque les ressources en eau sont insuffisantes ou que leur qualité est mauvaise. Dans le cadre de la production d'eau potable, cette méthode constitue une étape dans le processus de purification de l'eau permettant d'éviter un prélèvement direct des eaux de surface. La purification de l'eau s'effectue d'une part par filtration physique et d'autre part par le biais de processus chimiques comme la précipitation, la sorption, et la (bio)dégradation de substances indésirables. Ces processus sont généralement étroitement liés aux conditions d'oxydoréduction. L'activité des micro-organismes et les réactions chimiques qui en résultent modifient les conditions redox, lesquelles contrôlent à leur tour la présence de certaines substances dans l'eau et donc sa qualité. Les polluants les plus courants auxquels il faut faire face dans les eaux de surface sont les composés organiques (comme les résidus pharmaceutiques ou les pesticides), les agents pathogènes et les métaux lourds.

L'objectif du présent rapport est d'introduire les bases théoriques du zonage redox dans les bassins d'infiltration et de passer en revue les publications à la recherche de méthodes intéressantes permettant de contrôler les conditions redox. Ceci pourrait alors servir de base pour d'autres expériences de laboratoire ou à l'échelle du pilote dans le cadre du projet OXIRED.

La « zonation redox optimale » pour une élimination maximale des substances dépendantes de l'oxydoréduction a pour objectif de définir des temps de séjours optimaux sur la base de la cinétique de dégradation des contaminants dans l'eau souterraine. Si l'eau brute ne contient pas des substances ou des groupes de substances à fort taux d'élimination dans des conditions anaérobies à une concentration supérieure à celle autorisée pour l'alimentation en eau potable, les conditions anoxiques et anaérobies doivent être évitées pour ne pas mobiliser le fer ou d'autres éléments inorganiques en traces. On obtient d'excellents résultats au bout de 30 jours pour l'écoulement souterrain aérobie et au bout de 100 jours pour l'écoulement souterrain anoxique/aérobie. On constate néanmoins une amélioration significative de l'élimination des substances ou groupes de substances sensibles à l'oxydoréduction au bout de 15 jours pour l'écoulement souterrain aérobie et au bout de 2 jours pour l'écoulement souterrain anoxique/anaérobie.

Les facteurs principaux de la zonation redox dans les systèmes de recharge artificielle des nappes phréatiques sont la disponibilité en agents oxydants (l'oxygène ou le nitrate), en agents réducteurs (matières organiques, phases minérales réduites), en nutriments, ainsi que l'activité biologique (dans les bassins d'infiltration et dans le sous-sol) et le temps de séjour. Ces facteurs sont quant à eux liés à de nombreuses variables résultant des conditions naturelles, des conditions spécifiques au site (exogènes), et des conditions de mise en application des processus et des décisions. Les variables exogènes concernent notamment la géochimie de l'aquifère, la température ou l'alimentation naturelle des nappes phréatiques, tandis que les variables décisionnelles concernent des éléments tels que la géométrie des bassins, la distance entre le bassin et le puits, la profondeur du puits, le débit de pompage, etc.

S'il existe en théorie une large palette de possibilités permettant d'adapter le bassin d'infiltration, la zone hyporhéique et l'écoulement souterrain, seule une poignée d'entre elles est techniquement réalisable, dont notamment le contrôle de l'ensoleillement et de la température dans les bassins d'infiltration et les sédiments de surface, ainsi que le contrôle du mouvement de l'eau dans les bassins afin d'éviter la formation excessive d'algues au cours de l'enrichissement de l'eau en oxygène. Il est également possible d'ajouter des nutriments, ou au contraire de ne pas en apporter, puisqu'ils ont un impact sur la production de la biomasse. Il est aussi possible d'utiliser des matériaux de filtrage spécifiques avec du carbone organique en quantité et aux caractéristiques bien définies,

qui servirait d'accepteur d'électrons. Il est également possible de contrôler les taux d'infiltration en adaptant la charge hydraulique pour renforcer la formation d'une zone non saturée. Plus loin en aval, il est envisageable d'utiliser des substances contrôlant l'oxydoréduction via les puits d'injection et d'en surveiller le temps de séjour en régulant les débits de pompage ou en créant des puits à barrière hydraulique à différentes distances du bassin d'infiltration. Sur les systèmes de réalimentation artificielle récents, la conception (géométrie du bassin, distance entre le bassin et le puits, profondeur du puits) pourrait être optimisée en tenant compte de la zonation redox, dans la mesure où les autres exigences (essentiellement des taux de production suffisants) sont remplies.

Aucun exemple de contrôle redox dans les bassins d'infiltration n'a pu être identifié. Par conséquent, nous décrirons ici deux exemples de mesures visant à contrôler l'oxydoréduction : le « BIOXWAND® », un système de ré-oxydation artificielle d'un aquifère pollué et enfin le « Vyridox » et le « Nitridox », deux systèmes permettant d'injecter des eaux traitées de façon à influer les conditions redox dans l'aquifère.

Kurzfassung

Die künstliche Grundwasseranreicherung (GWA) mittels Infiltrationsbecken wird weltweit genutzt um Grundwasserressourcen im Falle ungenügender Grundwasserquantität oder –qualität zu ergänzen. Im Rahmen der Trinkwassergewinnung wird GWA häufig für eine naturnahe Aufbereitung angewendet, um die direkte Oberflächenwasserentnahme zu vermeiden. Neben der physikalischen Filtration umfasst die Aufbereitung bei der Untergrundpassage vor allem (bio-) chemische Reaktionen wie Fällung, Sorption und Abbau. All diese Prozesse sind eng mit dem Redoxmilieu verbunden. Es sind vor allem die Aktivität von Mikroorganismen und assoziierte Redoxreaktionen, die die Löslichkeit von vielen Substanzen beeinflussen, und somit auch die Wasserqualität. Typische Problemstoffe, die in Oberflächenwasser auftreten und durch die Untergrundpassage möglichst eliminiert werden sollten, sind organische Spurenstoffe, (wie z.B. Pharmazeutika oder Pestizide), pathogene Keime oder Schwermetalle.

Das Ziel dieses Berichtes ist es, über theoretische Grundlagen der Redoxzonierung in Infiltrationsbecken und über relevante Publikationen zu berichten, die anwendbare Methoden zur Redoxsteuerung in diesem Bereich beschreiben. Dies soll als Basis für Labor- und Freilandversuche dienen, die im weiteren Verlauf des OXIRED Projektes durchgeführt werden.

Das Konzept der “optimalen Redox Zonierung” für maximale Entfernung von redox-abhängigen Substanzen hat zum Ziel auf der Basis bekannter Abbaukinetiken optimale Aufenthaltszeiten innerhalb bestimmter Redoxzonen zu definieren:

Fall A (Substanzen oder Substanzgruppen, die bevorzugt unter anoxischen bis anaeroben Bedingungen abbaubar sind treten im Oberflächenwasser nicht in trinkwasserrelevanten Konzentrationen auf): anoxische bis anaerobe Bedingungen sollten generell vermieden werden, um geogenes Eisen und Mangan nicht zu mobilisieren.

Fall B (redoxsensitive Problemstoffe treten in trinkwasserrelevanten Konzentrationen auf): Einen maximalen Effekt aerober Untergrundpassage ist nach 30 Tagen erreicht, für anoxische / anaerobe Untergrundpassage nach 100 Tagen. Jedoch können bereits 15 Tage aerobe und 2 Tage anoxische / anaerobe Untergundaufenthalt zu einem deutlichen Rückgang redoxsensitiver Substanzen oder Substanzgruppen führen.

Die Haupttreiber für die Redoxzonierung in der GWA sind die Verfügbarkeit oxidierender Substanzen (Sauerstoff, Nitrat), von reduzierenden Substanzen (organische Substanz, reduzierte Mineralphasen wie Pyrit), von Nährstoffen sowie die biologische Aktivität (im Infiltrationsbecken sowie im Untergrund) und die entsprechende Aufenthaltszeit. Diese Treiber werden wiederum durch eine Vielzahl natürlicher, standort-spezifischer (exogener) und beeinflussbarer (Entscheidungs-) Variablen bestimmt. Exogene Variablen sind z.B. die Geochemie des Grundwasserleiters, die Temperatur oder die Grundwasserneubildung, während Entscheidungsvariablen Parameter wie die Geometrie des Infiltrationsbeckens, die Entfernung zwischen Becken und Brunnen sowie Brunnentiefe und Pumprate beinhalten. Obwohl theoretisch diverse Möglichkeiten bestehen, das Infiltrationsbecken, die hyporheische Zone und die Untergrundpassage zu modifizieren, sind nur wenige technisch auch machbar. Diese wären z.B. die Einschränkung der Sonneneinstrahlung und Temperatur im Becken sowie in den ersten Zentimetern Bodenpassage, die Kontrolle der Wasserbewegung innerhalb des Beckens, um Algenwachstum zu vermeiden, während das Wasser mit Sauerstoff angereichert wird. Aus demselben Grund könnten Nährstoffe reguliert werden um die Biomassenproduktion zu beeinflussen. Spezielles Filtermaterial könnte eingesetzt werden, mit einem definierten Gehalt und einer festgelegten Zusammensetzung von organischem Kohlenstoff, der als Elektronenakzeptor fungiert. Infiltrationsraten können durch die Anpassung des hydraulischen Potentials kontrolliert werden, um die Bildung

einer ungesättigten Zone zu fördern. Im weiteren Abstrom könnten Redox-kontrollierende Substanzen durch Injektionsbrunnen appliziert werden und durch die Anpassung von Pumpraten oder die Installation von hydraulischen Barrieren könnten die Aufenthaltszeiten kontrolliert werden. Für neue GWA Standorte wäre eine Optimierung der Beckengeometrie, der Entfernung zwischen Becken und Brunnen sowie der Brunnentiefe im Hinblick auf eine möglichst günstige Redoxzonierung denkbar, solange den Anforderung des Betriebs (hauptsächlich die Sicherstellung einer ausreichenden Entnahme) genügt wird.

Bislang wird in der Litertur nicht über eine Steuerung von Redoxzonen in Infiltrationsbecken berichtet. Es sind jedoch Bespiele dokumentiert, in denen das Redoxpotential im Grundwasserleiter selber manipuliert wird: als ersten Beispiel dient die Re-oxidation eines mit Ammonium kontaminierten Grundwassers (“BIOXWAND®”) und als zweites die Injektion von behandeltem Wasser, mit dem Ziel die Redoxbedingungen im Grundwasser für eine Eisenoxidation bzw. Nitratreduktion zu verändern (“Vyridox” und “Nitridox”).

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Thank you!

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Abbreviations

AR	aquifer recharge
BF	bank filtration
BOM	bulk organic matter
DOC	dissolved organic content
MAR	managed aquifer recharge
POC	particulate organic matter

Chapter 1
Introduction

1.1 Background

Managed Aquifer Recharge (MAR) is an umbrella term for different methods that induce the infiltration of water into an aquifer with the aim to enhance groundwater quality or availability. It is a possible countermeasure against groundwater overexploitation, that has been implemented in many parts worldwide. Although not generating "new" water resources, it enables the use of alternative resources that would not be used otherwise (e.g. storm-water, re-cycled water) for drinking water and irrigation by buffering high variations in availability and demand and by acting as an additional purification step [WssTP 2009].

Aquifer recharge via infiltration ponds is one of the most common MAR schemes applied in Europe. This scheme can be divided into four major elements (Figure 1):

- infiltration pond
- hyporheic zone
- subsurface passage
- production well

Bank Filtration (BF) is a closely related concept where riverbanks are used instead of infiltration ponds. Appendix A gives a detailed description of the different elements of an AR system.

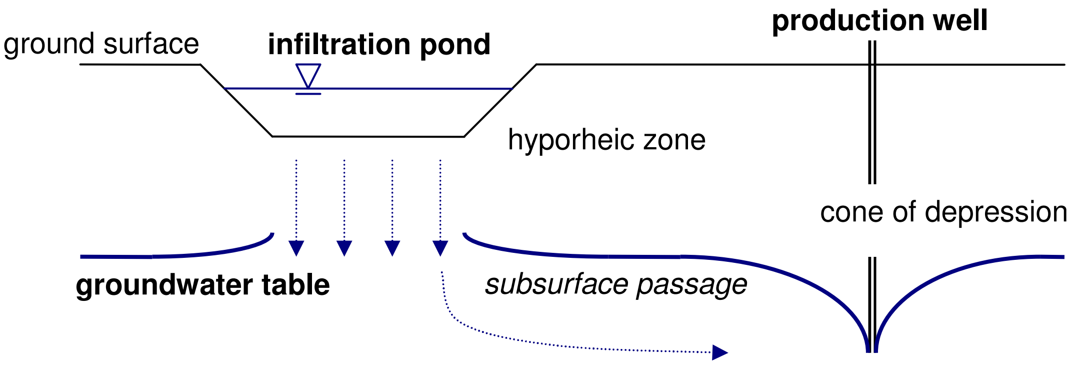

Figure 1: Typical Artifical Recharge (AR) system.

During subsurface passage different physical, chemical and biological processes take place which usually lead to an improvement of water quality. While the first two mentioned processes are only indirectly influenced by redox processes, biological degradation is a major driver for redox zonation and in turn is also highly influenced by redox conditions. An introduction to micro-organisms in the subsurface is given in Appendix B.

1.2 Redox Processes and Redox Zonation

During redox reactions, electrons are transferred between chemical substances and compounds. Because in real systems free electrons do not occur oxidation and reduction always need to be considered in a redox reaction:

Half reaction 1: oxidation Red1 => Ox1 + e$^-$
Half reaction 2: reduction Ox2 + e$^-$ => Red2

Redox reaction: Red1 + Ox2 => Ox1 + Red2 (1)

Neither oxidant nor reductant need to be neutrally charged. The occurrence of a redox reaction is controlled by the Gibbs free energy of the system. Gibbs free energy G of the system basically is a thermodynamical value which was mathematically constructed to describe the behaviour of a system. While ΔG = 0 constitutes chemical equilibrium any reaction yielding a ΔG < 0 will take place spontaneously because it allows the system to reduce its energy and therefore increase its thermodynamic stability. For a redox reaction $wB_{red} + xC_{ox} \Rightarrow yD_{ox} + zG_{red}$ the application of the law of mass action, Gibbs free energy G and ΔG = nFE yields the Nernst-Equation:

$$E = E° + \frac{RT}{nF} \cdot \ln\left(\frac{[D_{ox}]^y \cdot [G_{red}]^z}{[B_{red}]^w \cdot [C_{ox}]^x}\right)$$

[Apello & Postma 1996]

(2)

with: R = gas constant = 8.314 x 10^{-3} kJ/mol K
T = absolute temperature [K]
n = number of transmitted electrons
F = Faraday's constant = 96.42 kJ/V.g
E° = standard potential for standard conditions [V].
E = potential [V] (also written as ΔE)
[ ] = concentration or chemical activity of compound in mg/L

The (redox) potential E is a specific indicator for the redox reaction taking place. Figure 2 gives an overview of yielded energy by common redox-reactions. Because in real systems a multitude of redox pairs occur a measured potential will always be an overlap of several redox reactions and therefore only a limited indicator for actual redox conditions. This is referred to as "mixed potential". In addition, determining the in-situ redox potential of groundwater is prone to deficiencies due to sampling and measuring errors.

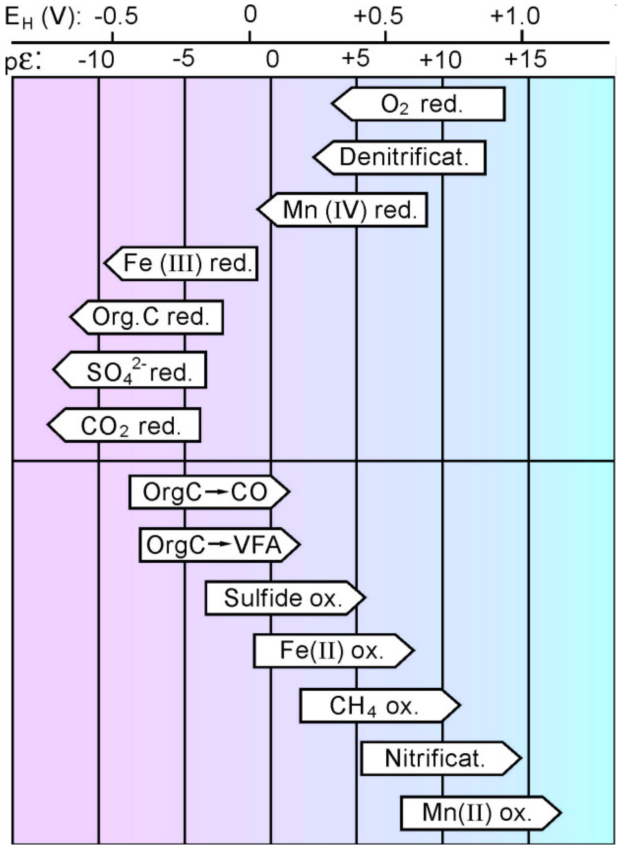

Figure 2: Redox potentials of typical redox reactions within natural systems [Stumm & Morgan 1981]

Several studies [Edmunds 1977; Edmunds et al 1984; Golwer et al 1970, 1976; Hack et al 1984; Jackson & Inch 1980; Jackson & Patterson 1982; Leuchs 1985, 1988, all cited after Mattheß 1994] have shown a zonation of hydrochemical properties within aquifers. Because this zonation largely reflects the predominant redox processes it is referred to as “redox zoning”. Following infiltration, conditions are usually aerobic as the infiltrating water has been in contact with the atmosphere. The formation of redox zones then commences as oxygen input is disabled (see chapter 1.5.3) and microbial activity leads to a successive depletion of electron donators such as oxygen, nitrate, Mn(IV), Fe (III) and sulfate along the flow path of the water, depending on the composition of the groundwater and the aquifer material. Different approaches to characterize the resulting redox zones are summarized in Figure 3.

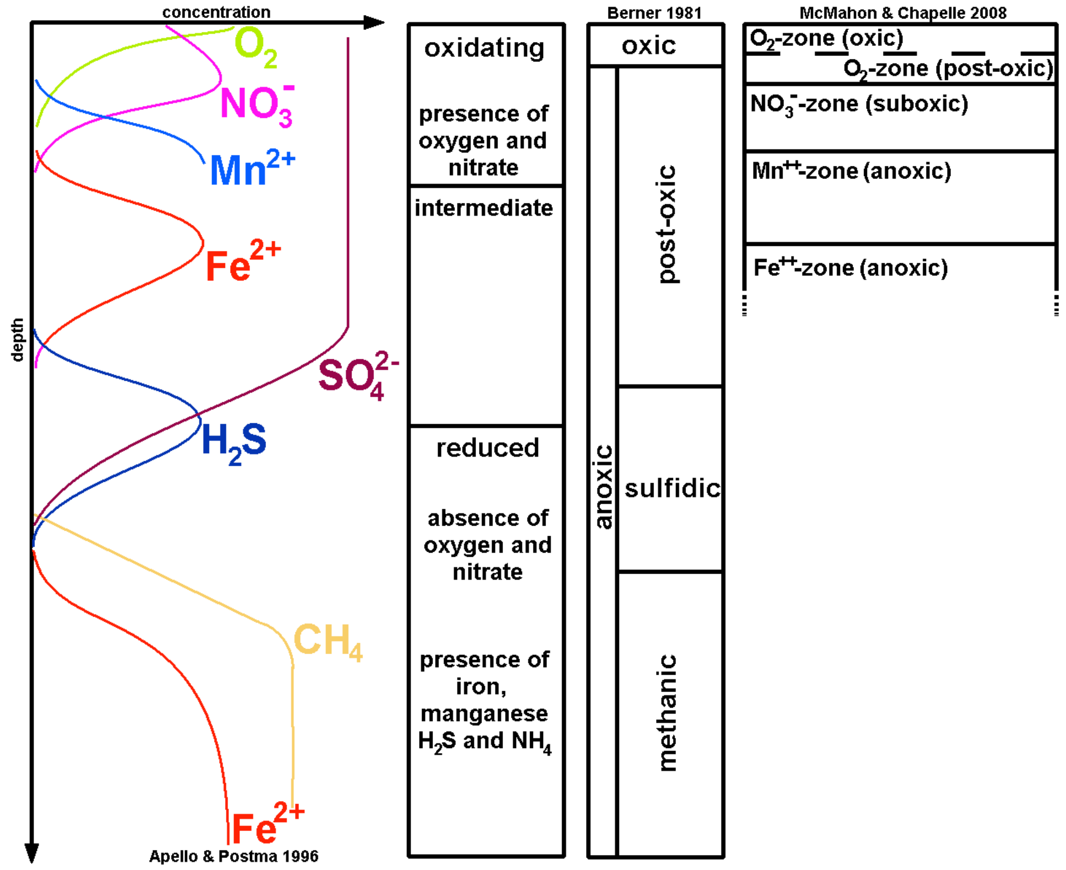

Figure 3: Schematic development of dissolved components with increasing depth and applied redox zoning concepts.

During artificial recharge, rarely all redox zones are developed (Figure 4). Therefore an approach that focuses on the oxidizing zone based on the classification by McMahon & Chapelle (2008) was introduced by [Wiese et al 2009] during the IC-NASRI project (Table 1).

Table 1: Classification of Redox Zones (based on [McMahon & Chapelle 2008]) applied for the interpretation of NASRI data [Wiese et al. 2009]

	redox species			
Redox zone	oxygen O_2 [mg/L]	Nitrate NO_3^- [mg/L]	Manganese Mn^{++} [mg/L]	Iron Fe^{++} [mg/L]
O_2-zone (oxic)	≥ 0.5	any	< 0.05	< 0.1
O_2-zone (post-oxic)	≥ 0.5	< 0.5	< 0.05	< 0.1
NO_3-zone (suboxic)	< 0.5	decreasing	< 0.05	< 0.1
Mn-Zone (anoxic)	< 0.5	< 0.5	≥ 0.05	< 0.1
Fe-Zone (anoxic)	< 0.5	< 0.5	any	≥ 0.1

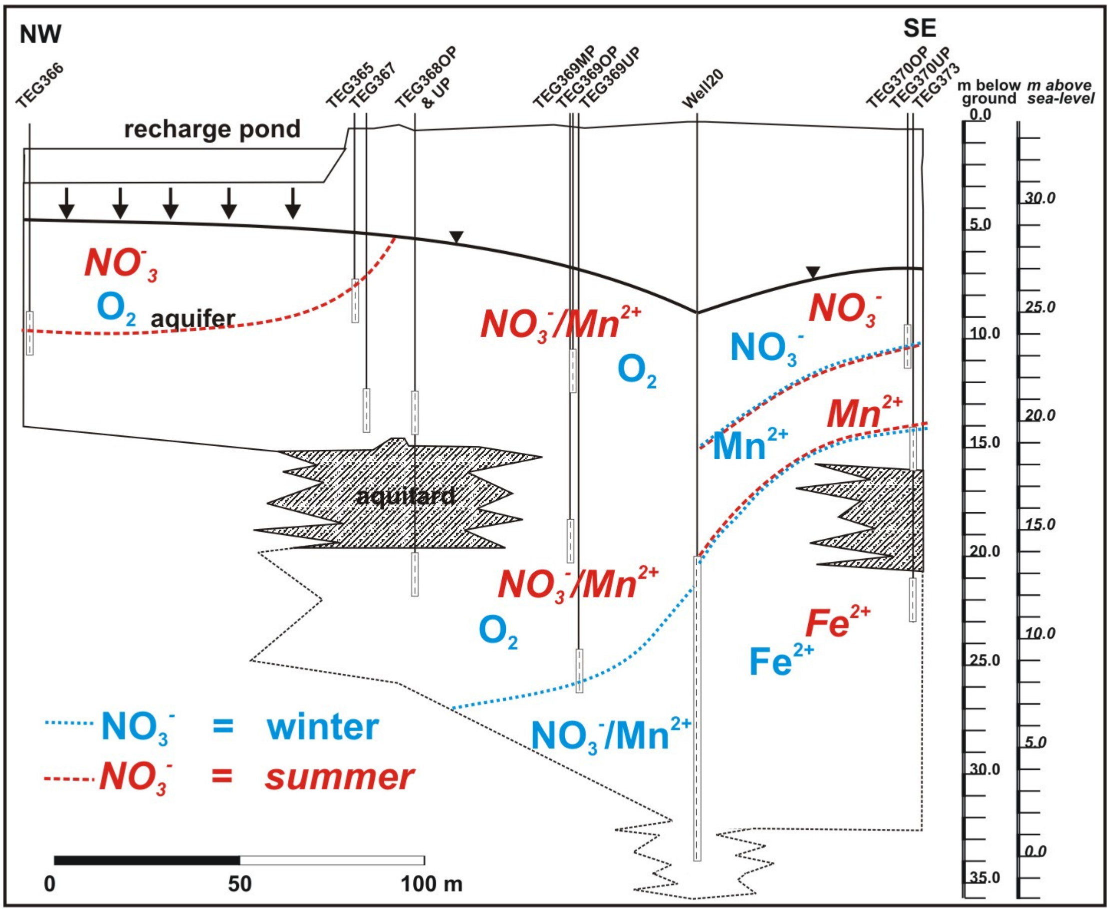

Figure 4: Redox zonation at the Lake Tegel AR pond in Berlin for summer (blue) and winter (red) according to Pekdeger et al. (2006).

Redox zoning may appear on macroscopic and microscopic scale. In addition, some zones may be missing. Detected oundaries between zones are usually rather diffuse which is due to the challenge of exact determination (see above). It should be noted that redox zonation is an idealization, assuming the occurrence of only one type of redox reaction. In reality several types of redox processes occur simultaneously with one type of reaction dominating (e.g. reduction of nitrate starts when oxygen concentrations reach approx. 0.5 mg/L [Huisman & van Haaren 1966, cited after Mattheß 1994]) and their predominant occurrence may shift over time.

Table 2 gives redox reaction typical for groundwater systems. A detailed description of the hydro- and geochemical processes that lead to redox zonation is given in Appendix C.

Table 2: Typical redox reactions within the system "aquifer" during AR [Mattheß et al 1994]

reaction	formula	oxidant	reductant	ΔG [kJ/mol]
aerobic respiration	$CH_2O + O_{2(gas)} => CO_{2(gas)} + H_2O$	oxygen	org. matter	-502,4
denitrification	$5CH_2O + 4\ NO_3^- => 2N_2 + 4HCO_3^- + CO_2 + 3H_2O$	nitrate	org. matter	-476,9
manganese-reduction	$CH_2O + MnO_{2(solid)} + 4H^+ => 2Mn_2+ + 3H_2O + CO_{2(gas)}$	MnO_2	org. matter	-304,4
Fe(III)-reduction	$CH_2O + 8H+ + 4\ Fe(OH)_{3(solid)} => 4\ Fe^{2+} + 11\ H_2O + CO_{2(gas)}$	$Fe(OH)_3$	org. matter	-116,0

1.3 Optimal Redox Zoning for Infiltration Ponds

Redox-dependent removal of substances during subsurface passage

An overview of substance groups relevant for drinking water treatment and their redox-dependent removal during subsurface passage as summarized in Grützmacher et al. (2010) is given in Appendix D. For many substances no redox dependency of removal can be observed (e.g. TSS, TDS, many trace organics). For pathogens, no field information is available, though laboratory experiments have shown that anoxic to anaerobic conditions may lead to less removal [Loveland et al. 1996] and [Jin et al. 1997].

Substances and substance groups that show enhanced removal under **oxic conditions** are:

- cyanotoxins (microcystins – for others no information is available),
- ammonium
- DOC
- some pesticides (ureas, penoxy-herbicides),
- many pharmaceuticals and x-ray contrast media (clindamycine, phenazone, propyphenazone, diclofenac, iopromide, AAA, AMDOPH, AMPH, DP, FAA),
- some other trace organics (1,7-NDSA, 2,7-NDSA)
- In addition, the mobilization of iron- and manganese as well as associated trace elements like arsenic is avoided.

Under **anoxic to anaerobic conditions** the following substances and substance groups show enhanced removal:

- nitrate
- most desinfection-byproducts (THMs)
- some pesticides (triazines)
- some pharmaceuticals and x-ray-contrast media (sulfamethoxazole, carbamazepine, AOI)

- chlorinated hydrocarbons (e.g. PCE, TCE)

Thus, the ideal redox zoning to target at a specific site clearly depends on the source water quality and the substances that need to be treated during subsurface passage.

Optimum residence times in specific redox zones

As the infiltrating water will usually be saturated with oxygen due to direct contact with the atmosphere in the infiltration pond, oxic conditions will usually prevail upon direct infiltration. If none of the substances or substance groups that show enhanced removal under anoxic to anaerobic conditions (e.g. nitrate, THMs) occur in source water at drinking water relevant concentrations a complete oxic passage should be targeted in order to avoid iron- and manganese mobilization and thus, further post-treatment.

Table 3 and Table 4 give an overview of substances and substance groups with redox-dependent removal characteristics and their respective degradation kinetics – where available – displayed as optimum residence times that were compiled from existing publications and own data.

Table 3: Time-dependent removal under oxic conditions.

Substance / substance group	**Residence time under oxic conditions**		
	for up to 25 % removal	**for up to 50 % removal**	**for 99 % removal**
cyanobacterial toxins (microcystins)	no information	no information	> 9 d*
ammonium	> 3 d***		
DOC	> 2 d**	> 30 d** (for high DOC not possible)	not possible
some pesticides (ureas, phenoxy-herbicides	no time-dependency reported		
PhACs and x-ray contrast media			
clindamycine	> 2 d***	> 3 d***	> 25 d***
diclofenac	> 10 d***	> 23 d***	> 200 d***
iopromide	no information	> 7 d+	no information
phenazone	no information	> 2 d+	no information
propyphenazone, AAA, AMDOPH, AMPH, DP, FAA	no time-dependency reported		
other trace organics (1,7-NDSA, 2,7-NDSA)	no time-dependency reported		
inorganic trace elements	Fe and Mn will be mobilized as soon as anoxic conditions prevail (and Fe and Mn are available in the sediment)		

* Grützmacher et al. (2007)

** Lenk et al. (2005)

*** NASRI data from Berlin (Pekdeger et al. 2006 and Wiese et al. 2010)

+ Stuyfzand et al. 2007

For substances and substance groups with enhanced removal under oxic conditions (Figure 5), an optimum travel time in the oxic zone would be 30 d. After that diclofenac is the only substance for which additional travel time would create additional benefit (phase D). If a residence time of 30 d can not be established, a minimum of 5 days should be achieved, in order to obtain a relevant decrease in DOC, algal toxins, ammonium and pharmaceuticals (phase A). After 15 days maximum removal of microcystins, iopromide and phenazone is achieved and a further decrease in clindamycine, diclofenac and DOC concentration.

Table 4: Time-dependent removal under anoxic to anaerobic conditions.

Substance / substance group	**Residence time under anoxic to anaerobic conditions**		
	for up to 25 % removal	**for up to 50 % removal**	**for 99 % removal**
nitrate			> 2 d (> 97 % removal)*
disinfection by-products (THMs)	< 20 d**	> 20 – 40 d**	> 100 d**
some pesticides (triazines)	no time-dependency reported		
PhACs and x-ray contrast media			
sulfamethoxazole,	> 20 d***	> 40 d***	> 80 d***
carbamazipine,	no time-dependency reported		
AOI	no time-dependency reported		
highly soluble chlorinated hydrocarbons (PCE)	no time-dependency reported		

* NASRI data from Berlin (Grützmacher et al. in prep).
** adapted from Schmidt et al. (2003)
*** NASRI data from Berlin (Wiese et al. 2010)

Under anoxic to anaerobic conditions (Figure 6) very short travel-times (2 d) may already remove most of the nitrate present (zone A). After about 100 d complete removal of THMs and sulfamethoxazole can be expected (zone B). Based on the available references further residence time (zone C) does not lead to further quality improvement.

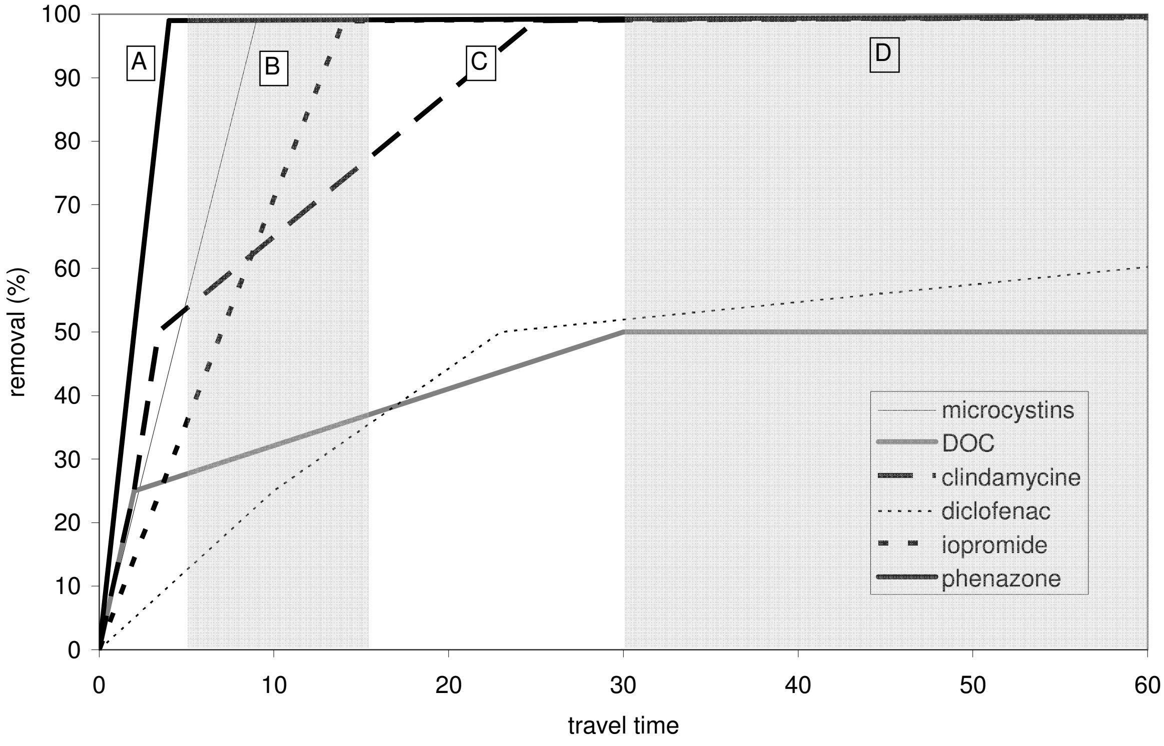

Figure 5: Schematic travel-time dependent removal for substances and substance groups that show enhanced removal under oxic conditions (zones A to D: see text).

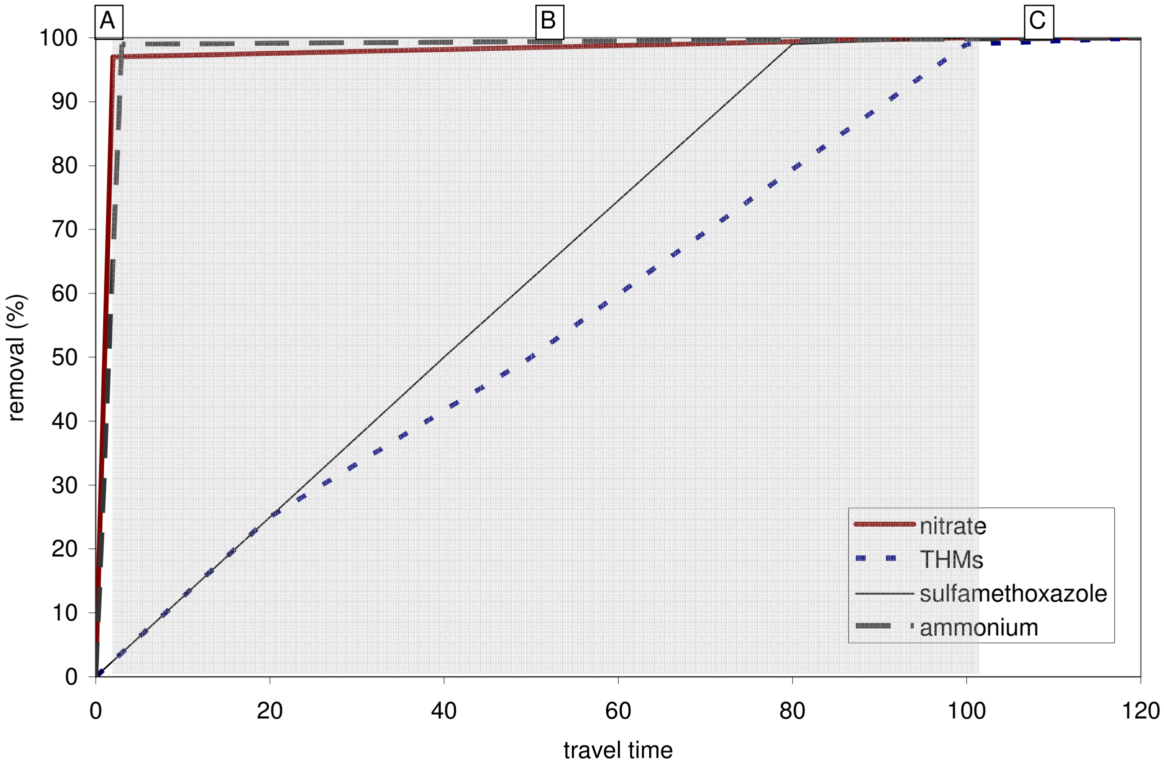

Figure 6: Schematic travel-time dependent removal for substances and substance groups that show enhanced removal under anoxic to anaerobic conditions (zones A to C: see text).

Summary Chapter 1

During artificial recharge of groundwater redox reactions and the resulting redox zonation play a decisive role in determining the water quality of the produced water. A classification following McMahon & Chapelle [2008] is best suited to describe redox zonation in AR systems: oxic zone (presence of O_2), sub-oxic zone (no oxygen but nitrate present), anoxic zone (Fe- and Mn reducing zones).

The optimal redox zonation for maximum removal of redox-dependent substances or substance groups should be determined based on the contaminants present in the source water. However, there are some general statements that can be made:

- Anoxic to anaerobic conditions are of benefit only if certain substances or substance groups need to be removed during subsurface passage (nitrate, most desinfection-byproducts (THMs), some pesticides (triazines), some pharmaceuticals and x-ray-contrast media (sulfamethoxazole, carbamazipine, AOI) or chlorinated hydrocarbons (e.g. PCE)). If these substances are not present in the source water (at relevant concentrations) anoxic to anaerobic conditions may be avoided in order not to mobilize iron and manganese (and other related inorganic trace elements).
- Maximum benefit for aerobic subsurface passage is reached after 30 d, for anoxic / anaerobic subsurface passage after 100 d.
- 15 d of aerobic and 2 d of anoxic / anaerobic passage already lead to substantial removal of redox-sensitive substances or substance groups. A minimum of 5 d for aerobic subsurface passage is recommended in order to achieve a relevant effect for most of the regarded substances or substance groups.

Chapter 2
Drivers for Redox Processes and Possible Manipulations

2.1 Main Drivers for Redox Processes

The main drivers for redox processes in the subsurface during artificial groundwater recharge are summarized in Table 5 and described below.

Table 5: Summary of drivers for redox processes and the influencing exogenous and decision variables.

topic	drivers	main redox-related process	influcencing exogenous and decision variables
hydro-geochemistry (infiltrating water, ambient groundwater and aquifer material)	availability of oxidizing agents (oxygen and nitrate)	respiration, denitrification	aquifer geochemistry (organic matter, mineral phases), temperature, natural gw recharge, presence & thickness of unsaturated zone, water table oscillations
	availability of reducing agents (organic matter and mineral phases)	reduction of oxygen and nitrate, pyrite oxidation	geochemistry of infiltration basin material, aquifer geochemistry, mixing with ambient groundwater
biological activity	bacteria in the subsurface	respiration	temperature, nutrients (C, N, P, K, DOC), pH
	algae in the infiltration pond	DOC consumption, O_2 production	temperature, sunlight, nutrients
hydraulic characteristics	residence time	reaction kinetics of redox reactions	well field geometry, distance pond to production well, pumping rate, hydraulic conductivity of aquifer and clogging layer, presence & thickness of unsaturated zone, temperature (water viscosity), retardation coefficient

2.1.1 Hydro-Geochemistry of the System

A pre-requisite for every reaction is that it can only include reactants present in the system, thus oxidizing and reducing agents need either to be available in the infiltrating water, in the aquifer matrix or in the ambient groundwater.

Availability of Oxidizing Agents (Oxygen and Nitrate)

The oxygen content of AR systems is controlled by three factors:

1. concentration in the source water
2. additional input of oxygen through the unsaturated zone
3. consumption of oxygen, especially by oxidation of organic matter or reduced mineral phases (e.g. pyrite)

Ad 1): The source concentration is **temperature** dependent and increases with decreasing temperatures. A dependency of oxygen concentration on pressure can be expected but is negligible since infiltration usually occurs at atmospheric pressure (higher pressures could occur e.g. if oxygen is injected into the aquifer). The maximum concentration of oxygen within the surface water is 15.4 mg/L at 0 °C and atmospheric pressure (see figure 3 in 1.3.3). Surface water can contain 9 to 14.4 mg/L oxygen for temperatures between 20 °C and 0 °C when at equilibrium with the atmosphere [Gerb 1953, cited after Mattheß 1994, p.155]. Oxygen-solubility decreases with rising temperature (see Figure 4).

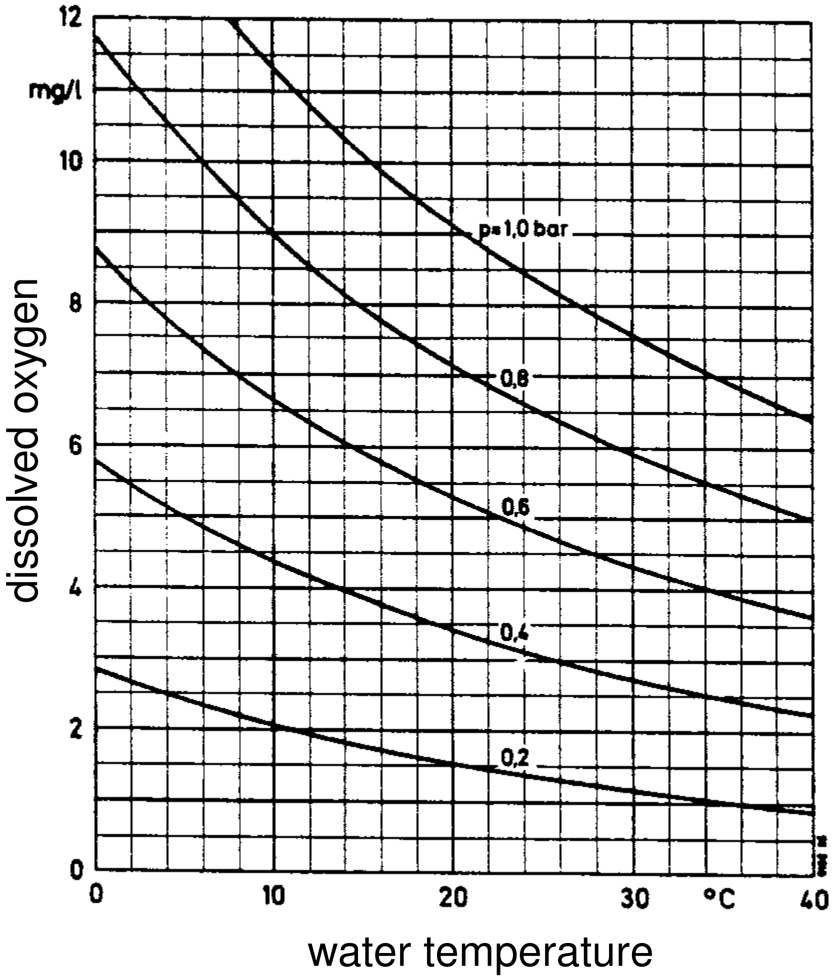

Figure 7: Solubility of oxygen for different temperatures and pressures [Balke et al. 2000, p.468]

Ad 2): For oxygen the system "subsurface passage" is semi-closed with input of oxygen limited to two types: source input and input through the unsaturated zone. The latter includes dissolved oxygen penetrating with the percolation of recharging water (i.e. **natural groundwater recharge**), diffusion of gaseous oxygen through the **unsaturated zone.** In both cases, the input is controlled by Henry's Law.

Ad 3): Since oxygen may react with any other compound in redox reactions [Apello & Postma 1996 p.262] it is used as oxidizing agent for the oxidation of organic compounds and reduced mineral phases (e.g. pyrite). The decrease of oxygen concentration is therefore connected to the **amount of organic content and reduced mineral phases** present in the aquifer.

Availability of Reducing Agents (Organic Matter and Reduced Mineral Phases)

Organic compounds are the major reducing agent within subsurface systems. In theory, organic content should be decreasing with time, however these changes are small compared to the natural variations observed. Organic compounds comprise i) **organic aquifer material** (particulate organic carbon - POC) and ii) particulate and dissolved organic compounds (POC and DOC) introduced with the infiltrating water.

On the basis of their degradability three categories of dissolved organic matter are distinguished [Gimbel et al 1992, cited after Jekel et al 2006] cf. Figure 8:

- easily degradable
- medium to poorly degradable
- not degradable

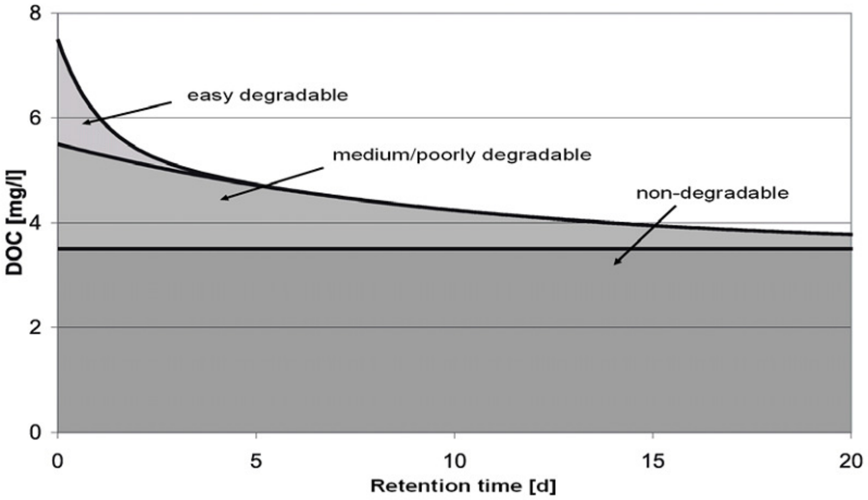

Figure 8: Three categories of DOC [Gimbel et al 1992] with regard to retention time.

A balance study, carried out with NASRI-Data from Berlin, focused on the relation between oxygen decrease and the change of organic content [Jekel 2006]. By using a column study a mean oxidation number (MON), describing the amount of oxygen consumed during mineralization of one milligram of organic carbon was deduced. For natural surface water a MON of 2.5 to 3 was derived. Using this value and concentrations of oxygen, nitrate and DOC of the water before and after the column passage, degradation of POC from the sediment could be evaluated by a mass balance model. Decrease of oxygen and nitrogen concentration equals a certain change of (D)OC concentration in the water. Any difference between the calculated (D)OC concentration and input DOC has to be attributed to degradation of POC. It was found that no significant mineralization of POC took place in the column – due to the fact that the quartz sand used for the experiments did not contain any organic matter apart from the biofilm that had formed during the experiments. The same principle was then applied to a BF site at Lake Tegel in Berlin. Here a degradation of POC did occur. In addition, dissolution of $CaCO_3$ was found to be a relevant process. Figure 6 shows all processes that were included in the calculation as well as assumed sediment properties [Jekel 2006].

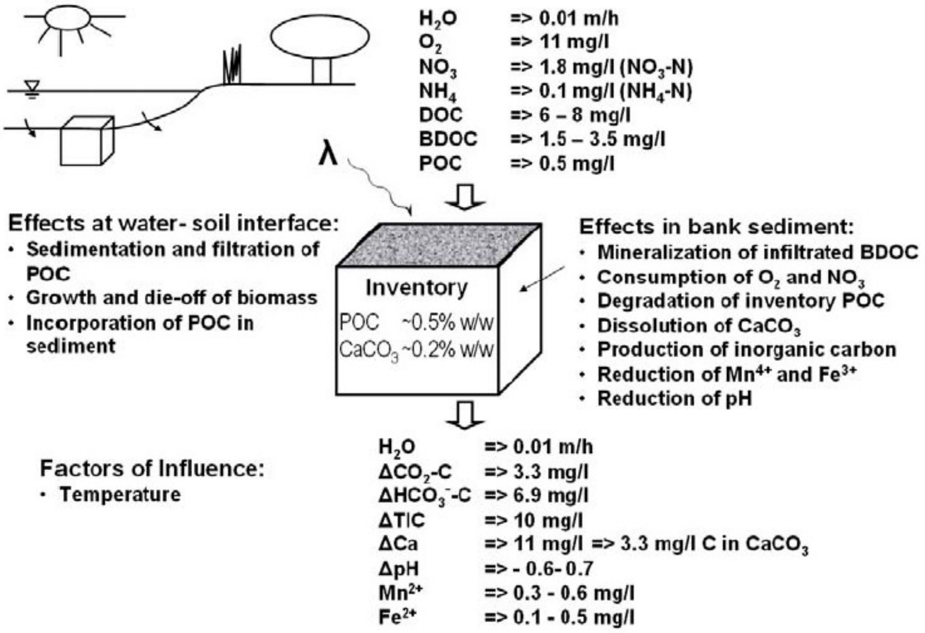

Figure 9: Parameters for mass balance model at Lake Tegel BF [Jekel 2006]

Figure 6 shows the mass balance data. Calculations were made for a sediment cube of 1 m^3 situated directly at the water-soil-interface. Oxygen was completely consumed. The carbon balance shows an increase of OC that has to be attributed to the processes consuming the oxygen, contrary to the expected decrease [Jekel 2006]. This means that POC and DOC are mobilized from organic carbon naturally occurring within the sediments [Gunkel & Hoffmann 2009].

Table 6: Mass balance model of oxygen and carbon during infiltration [Jekel 2006]

oxygen balance		carbon balance	
input [mg/L]		input [mg/L]	
O_2 in infiltrating water	~ 11.0	BDOC in infiltrating water	~ 2.5
O_2 equivalent in infiltrating NO_3^-	~ 6.1	POC in infiltrating water	~ 0.5
		POC in sediment inventory	~ 3.2
		Carbon from $CaCO_3$-dis.	~ 3.3
sum	~ 17.1	sum	~ 9.5
consumption [mg/L]		output [mg/L]	
O_2 for BDOC miner.	~ 6.8	Carbon in ΔCO_2	~ 3.3
O_2 for water POC miner.	~ 1.3	Carbon in ΔHCO_3^-	~ 6.9
O_2 for nitrification	~ 0.35		
O_2 for POC miner.	~ 8.7		
sum	~17.15	sum	~10.2

For the reduction of oxygen and nitrate, the sulfur bearing mineral pyrite is a competing reducing agent for the organic content [Prommer & Stuyfzand 2005].

For sandy sediments at the "Segeberger Forst" (Forest of Segeberg) in the North German Plain POC was found to represent 0.6% of the sediment. This value equals 11.1 g of organic carbon within one kilogram of sediment [Griebel & Mösslacher 2003, p.64]

Since the subsurface passage constitutes an open system, mixing with ambient groundwater is unavoidable. It can be assumed that, due to other flow paths and longer residence times, the water generally is more reduced.

2.1.2 Biological Activity

Redox processes are catalysed by bacteria. Bacterial activity seems to be correlated with **temperature**. A deep well injection experiment, where oxygenated water was injected into a deep aquifer to exclude interactions of the water and the aquifer with the atmosphere, found that detection of oxygen at the production wells only occurred for temperatures below 14 °C [Prommer & Stuyfzand 2005] (see also chapter 3.3). Since oxygen is the first substance to be reduced by bacteria it can be assumed that (significant) bacterial activity (consumption of oxygen) only occurs for (water) temperatures above 14 °C. Similar findings were reported for the AR pond at Lake Tegel [Greskowiak et al. 2005]. Therefore, a threshold temperature for bacterial activity can be assumed.

Other parameters that influence the biological activity are **organic content** and **nutrient concentrations** [Massmann et al 2006b]. Bacteria convert organic content to gain energy, therefore larger quantities of organic content can support larger populations of bacteria inducing larger bacterial activity assuming sufficient supply of nutrients. Correspondingly low organic content equals scarce bacterial population. Below threshold concentrations the die-off-rate exceeds the formation of new bacteria and therefore causes bacterial activity to cease [Mattheß 1994, p.188]. Only sufficient concentrations of organic content will allow a build-up of larger populations of bacteria metabolizing the organic content.

Algae in the surface water body are also able to convert DOC into biomass. Algal DOC-consumption is approx. 5 to 60% that of bacteria. Sunlight proved to be a major influence factor in algae activity [Tittel et al 2009], [Kamjunke & Tittel 2009]. Vertical distribution of algae is limited by the penetration of light into the interstices. Side effects of algae are the dissipation of algal toxins and an increase of pH through photosynthesis. Algae create a daily cycle of oxygen concentration because they produce and consume oxygen, resulting in oxygen enrichment during the day and depletion during the night. This may cause a (critical) low oxygen concentration during night time. Because of their production of extra-cellular polymeric substances, they bear a strong influence on clogging processes [Gunkel & Hoffmann 2009].

2.1.3 Hydraulic characteristics

Because redox reactions are time dependent, the **residence time** is generally one of the most important controlling factors. It is influenced by flow path and flow velocity, therefore **hydraulic conductivity** of the subsurface (aquifer and clogging layer), the **pumping rate**, the **distance between infiltration pond and production well** as well as **well field geometry** are the main drivers. In addition, the **presence and thickness of an unsaturated zone** and the **temperature** play an important role.

A survey [Grützmacher et al. in prep.] conducted on data of 170 BF and AR sites worldwide found the following data:

- max. hydraulic conductivities ranging between 0.0001 m/s and 0.05 m/s with the majority of sites with a range between 0.00011 m/s and 0.0051 m/s
- average distance between infiltration bank and production well ranging between less than 50 m and more than 2000 m, the majority of sites had distances under 500 m
- flow times ranging between 1 and 4000 days, the majority of sites had flow times from 10 to 50 days

For AR sites in Berlin, the hydraulic conductivity was ranging between 1 x 10^{-5} and 1 x 10^{-3} m/s. These values are lower than average. Flow distances were ranging from 30 to 50 m, also below the average [Grützmacher et al. in prep.].

2.2 Possible Manipulation of Redox Drivers

For the parameters “biological activity” and “hydro-geochemistry” several applications have already been developed (see chapter 3). They are based on the idea of changing chemical conditions within the subsurface, usually to intensify or trigger purification processes.

Controlling the parameter “hydraulic characteristics” would allow an opposite approach: Utilization of the existing chemical conditions in the subsurface and increasing the water purification by prolonging the time in which reactions can take place. This could offer advantages like simplicity (changing the chemistry in the subsurface needs personnel qualified beyond taking simple measurements, the applications Vyredox and Nitredox are highly dependent on being run within specifications (see chapters 3.2 and 3.3)) , reduced costs (for the needed chemicals or their application to the groundwater) or ecological advantages (avoidance of side effects from applied chemicals, avoidance of waste products).

Four stages of AR have been identified in chapter 1: the infiltration pond, the hyporheic zone, the subsurface passage and the production well. Within these the stage “subsurface passage” exhibits the longest residence times with more or less stable conditions (contrary to the infiltration pond where constant and uncontrolled input from the atmosphere is possible and prone to significant changes in water chemistry). Therefore, with regard to the search for applications based on residence time, the subsurface passage is of prime interest.

While subsurface passage is an open system from a thermo-dynamical point of view, actual access is restricted because of its limited accessibility. Influence on the subsurface passage is restricted to/possible for:

- input via infiltration pond and hyporheic zone (<=> educt chemistry)
- pumping regime (<=> hydraulic control of the subsurface passage)
- additional input via wells during the subsurface passage (<=> reactants)

2.2.1 Manipulation of the Infiltration Pond

The used surface water is the first controllable parameter. While its composition is determined by the surface water system, the volume of an infiltration pond is small enough to actively influence the composition of the water within it. In addition, pre-treatment is often performed and could be adjusted to influence the redox conditions.

- Algae (and bacteria) may alter the water composition significantly (with regard to DOC) before the actual infiltration begins. The controlled growth of algae may be used to remove DOC since algae convert DOC into biomass which can be removed manually. The main problem with the use of algae are the occurrence of cyanobacteria and possibly also cyanotoxins. Some of them are easily degraded (e.g. microcystin-RR and –LR under oxic (aerobic) conditions within a few days) while others may be highly persistent (e.g. cylindrospermopsin) [Gunkel & Hoffmann 2009].
- Infiltration ponds are usually situated outdoors. Placing the pond "indoors" allows to control factors like temperature of the water and sunlight intake. This might offer possibilities to steer bacterial activity and algal growth.
- The formation of the clogging layer is partially controlled by the flow conditions within the infiltration pond. Keeping the water moving within the pond might reduce sedimentation of fine material and thereby increase the lifespan of the infiltration pond before redevelopment is necessary. The hydraulic pressure results from the water level within the pond and is responsible for infiltration rates. Therefore, the water level in the pond could be used to control infiltration rates and especially to compensate loss of hydraulic conductivity due to clogging towards the end of an operational cycle of an AR-pond.
- With regard to threshold concentrations specific compounds could be enriched to increase bacterial activity.

2.2.2 Manipulation of the Hyporheic Zone

The interface surface water/groundwater is an important step in the AR-process. It marks the beginning of closed system conditions for oxygen (until re-oxidation). Along the first meters of infiltration, the strongest biochemical (e.g. microbial) activity is encountered [Doussan et al 1997].

While it may constitute a very complex approach, an artificial aquifer (or at least an artificial hyporheic zone) might offer a wide range of advantages **beginning with**

controlled hydraulic conditions (which subsequent could allow control of travel times). DOC and chemical conditions could also be intentionally manipulated by application of organic content depending on oxygen and nitrate concentrations in the infiltrating surface water. Implementation of heating mechanisms might increase zones of desired bacterial activity. Since the bottom of the infiltration pond has to be redeveloped regularly and the application of a layer of sand is already common [Balke et al 2000 p.525], creating one or two meters of artificial sediments seems to be the next logical step.

A further possibility is not to increase the water residence time within the desired zone (usually oxic), but to enhance adsorption of target substances to the minerals present in the zone, thus prolonging their residence time and possibility for degradation. This concept could be followed by the addition of sorbing agents (e.g. **iron coated sands**) to the filter sand in the infiltration basis.

2.2.3 Input via Wells during Subsurface Passage

The production well itself, as the end of the subsurface passage, has little influence on the subsurface passage to affect redox processes. However, a series of wells along the flowpath away from the infiltration pond would allow a wide range of benefits.

The wells also would allow transferring any substance or phase into the system “subsurface passage”. This could be used for re-oxidation by pumping air into the wells or even a re-injection of water into a certain redox zone (if the produced water showed insufficient removal). There are already some applications using this principle (Vyredox, Nitredox, Bioxwand, see chapter 3).

A more important aspect is that every well can be used for monitoring of chemical properties. This is a prerequisite for any attempt to utilize residence times for water purification processes: the chemical conditions need to be known to deduce the necessary time for the desired water purification. The production of drinking water therefore could translate into the question from which well the water should be produced.

The control of the hydraulic regime could be improved by pumping at different rates in the wells, even though pumping is highly likely to decrease the travel time by increasing the gradient of the groundwater table. Injecting additional water would decrease the cones of depression and increase travel times.

Since water infiltrates radially in every direction away from the infiltration pond, a series of wells surrounding the pond might be able to control dilution with ambient groundwater by abstracting ambient groundwater before it reaches the area of the infiltrated surface water.

With infiltration systems like at Lake Tegel in Berlin, where three infiltration ponds are surrounded with production well galleries [Massmann et al 2006b], or Nitredox-waterworks (see chapter 3.2) where a production well is surrounded with several rings of injection and monitoring wells, the technical foundations for these kind of applications appear to be already present.

If already existing AR-systems exhibit too short travel times, permeability could to be reduced. This could be achieved by using the side effect of precipitation. The process Vyredox (see chapter 3.2) uses injection of oxygenated water into the subsurface to trigger precipitation of Iron and Manganese. Using different injection rates the oxidizing zone is moved through the subsurface causing a distribution of precipitations within the aquifer. Adaptation of this concept for a one-time use to tune hydraulic conductivity appears possible by infiltrating water with high concentrations of iron and manganese through the pond and injecting water with high concentrations of oxygen through the production well. The adaptation would require simulations and close monitoring of the process. In addition, precise specifications on which the AR-system would be run afterwards are necessary to prevent a remobilisation of the precipitated materials, which would negate the change of hydraulic conductivity and cause problems with the quality of the drinking water.

2.2.4 Planning of new AR-Systems taking Redox Zonation into Account

The previously described ideas can be implemented into existing AR-systems. These come with certain limitations like a fixed distance between the infiltration pond and the production well. A modification of this distance could be achieved by moving the pond or the well. This could be impossible due to lack of space in highly populated areas or due to costs.

In Berlin, where studies on AR and processes in the subsurface were conducted by Massmann and Greskowiak during the NASRI project, most waterworks were built a century ago using groundwater originating from bank filtration (see appendix 5) to which AR-systems were added since 1981 [BWB2]. Bank filtration as a water purification step has been used in Europe since 1810. For these and for the AR-sites that were added after decreases in water quality that begun or were first detected in the 1960s [Grützmacher et al. in prep.] obtaining sufficient water volumes was the major driver. This means that the layout of many existing AR-sites does not comply with the needed travel times to reach the desired water purification and results in additional purification processes performed after production of the water.

New challenges (e.g. emerging contaminants) have lead to more scientific research on the subject. This research (e.g. IC NASRI) resulted in better knowledge of substances and compounds in surface water as well as their degradation in the subsurface and the scope of necessary travel times.

In recent years, the ecological concern has grown significantly. Experience from industrialization in Europe and America might prevent similar environmental impacts in Asia or Africa. At the least, future decreases in surface water quality can be integrated into the planning of new AR-sites. Predictions on future development in water demand can be included to predict pumping rates, resulting in another planning parameter.

Computerization offers new possibilities to model groundwater and therefore better predict the behaviour of AR-systems.

A thorough exploration of the future AR-site should deliver the following data:

- chemical properties of the surface water (composition of the educt) and their temporal variability
- hydraulic properties of the subsurface in high resolution (to enable precise modelling of the groundwater flow)
- biological environment (to determine and extrapolate the capacity for redoxreactions of the subsurface)
- exact plans about how much groundwater volume is to be produced from the AR-system (to predict the cone of depression and its impact on the groundwater table)

Combining this information into a computer simulation could result in a precise model that can be used to tune the AR-layout (e.g. calculation of ideal distance between infiltration pond or riverbank to the production well to maximize water purification).

2.2.5 Conclusions and Further Investigations

Actual control of the redox potential and redox reactions appears hard to achieve. Little adjustments via wells seem possible. Attempts to control the flow of water through a given redox zonation with the help of wells appear very feasible. Optimization of the input water might offer additional help with regard to adjustments. Intensified measures regarding the pond bottom (e.g. iron coated sands) could yield control over the first meters of infiltration and therefore over the most influential stage of the AR-process with regard to water quality. The proposed measures create new questions:

- A study showed that aquifers may lose their ability to reduce compounds [Kunkel et al 1999] because substances causing reduction become depleted. Observed times for complete loss of denitrifying capacity varied between 90 a and 930 a. This raises the question if the subsurface passage needs regular phases of regeneration. A correlation between seasonal changes of infiltrating water, removal processes and aquifer regeneration should be investigated.

- To allow better planning of future AR-sites closer investigation of the “clogging layer” is necessary to enable prediction of the effect of re-development on infiltration rates.
- Costs and efficiency as well as the CO_2-footprint need to examined. Control of temperature might use up a lot of energy, surpassing the energy need of post-production treatment.
- Many of the proposed measures represent severe invasions into the natural aquifer and the recharge cycle (indoor infiltration pond, artificial hyporheic zone, well system). If these measures show to be feasible, would the next logical step, a completely artificial subsurface passage, create further improvement?

Summary Chapter 2

The main drivers for redox zonation in AR systems are:

1) Availability of oxidizing agents (oxygen, nitrate), influenced by aquifer geochemistry (organic matter, mineral phases), temperature, natural gw recharge, presence & thickness of unsaturated zone, water table oscillations
2) Availability of reducing agents (organic matter, reduced mineral phases), influenced by geochemistry of infiltration basin material, aquifer geochemistry, mixing with ambient groundwater
3) Biological activity (in infiltration pond and subsurface), influenced by temperature, nutrient availability and for infiltration ponds additionally sunlight.
4) Residence time, influenced by well field geometry, distance pond to production well, pumping rate, hydraulic conductivity of aquifer and clogging layer, presence & thickness of unsaturated zone, temperature (water viscosity), retardation coefficient

Possibilities for manipulation exist in different elements of the AR system:

1) Infiltration pond (e.g. controlled algal growth to decrease DOC, control sunlight and temperature, water movement, addition / avoidance of nutrients)
2) Hyporheic zone (e.g. control temperature, use of specific filter material with defined org. C or high adsorption capacity, control infiltration rates to enhance formation of unsaturated zone)

3) Subsurface passage (e.g. application of redox controlling substances via injection wells, controlling residence times by adjusting pumping rates or creating hydraulic barrier, wells at different distances from infiltration pond, manipulating hydraulic conductivities through precipitation)

For newly constructed AR systems the well field design could be optimized with respect to redox zonation, as long as other requirements are met.

Chapter 3
Applications and Examples for Redox Control Measures

This part of the paper presents attempts that are or have been made to control the redox potential to improve GW-quality. Accidental findings as well as studies/experiments are included.

3.1 BIOXWAND [Engelmann et al. 2004]

The BIOXWAND (“biox-wall”) represents an artificial re-oxidation of a polluted aquifer to induce the growth of bacteria removing the pollutants. The technique was used at the sewage treatment plant Münchehofe on the eastern border of Berlin, north of the Müggelsee within the „Berliner Urstromtal“, where a pollution with NH_4^+ occurred (due to decades of use as a sewage farm [BWB]). The pollution prevented the water to be used as drinking water by the waterworks Friedrichshagen on the northern shore of Lake Müggelsee [Engelmann et al 2004].

The basic principle of the technique is the creation of a „gaseous wall“ in the flow path of the groundwater by injection of gaseous oxygen (through wells). Due to the passage through the gaseous wall, the water is oxygenated. This allows aerobic bacteria to build up populations. The bacteria „Nitrosomonanas“ and „Nitrosolobus“ oxidize ammonium to nitrite:

$$2\ NH_4^+ + {}^3/_2\ O_2 \quad => \quad 2\ NO_2^- + 2\ H^+ + H_2O \qquad \text{(Mattheß 1994, p. 176)}$$

Afterwards the bacteria „Nitrobacter“ oxidize the nitrite to nitrate:

$$2\ NO_2^- + O_2 \quad => \quad 2\ NO_3^- \qquad \text{(Mattheß 1994, p.176)}$$

The effect of a spatially limited input of oxygen equals a groundwater-atmosphere-interface. Therefore, along the following flow path a common redox zonation establishes, facilitating the removal of nitrate and trace elements (as described in chapter 1). This is referred to as „reactive zone“. The thickness of the gaseous wall and the length of the reactive zone are solely controlled by the injection rate of oxygen.

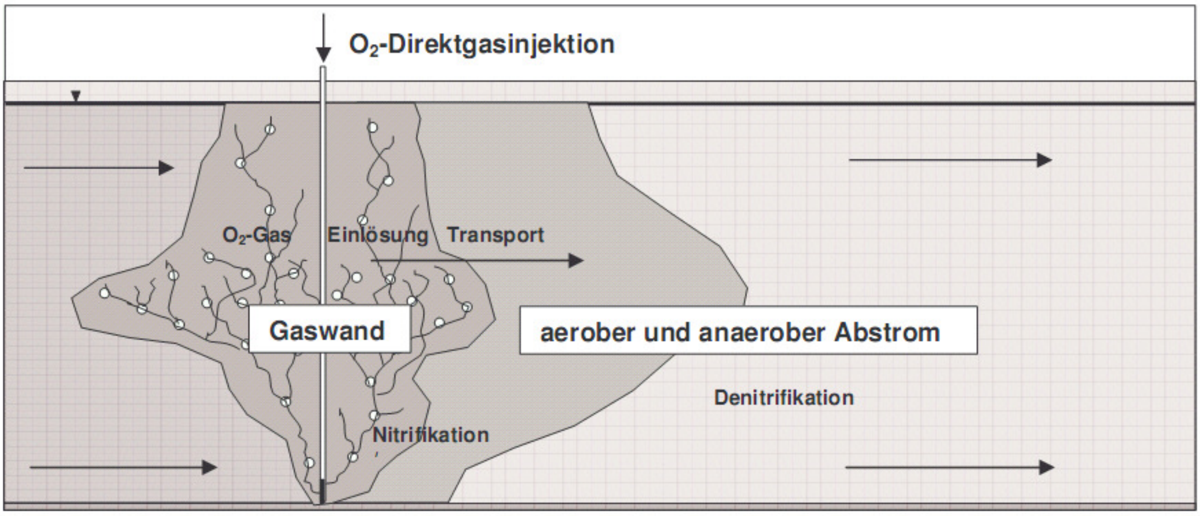

Figure 10: Schematic cross section of the BIOXWAND-process [Engelmann et al 2004]

After the injection of oxygen redox conditions within the aquifer changed rapidly within a matter of days. Within the gaseous wall the redox potential increased between 150 and 250 mV to a total value of 300 mV. A first increase of nitrite- and nitrate-concentrations was detected downstream of the injection in an interval of 30 days (areas with good supply with injected oxygen) to 60 days (areas with spare supply with injected oxygen) after the start of injection. The mean rate of nitrifcation was between $7*10^{-8}$ kgN/kg*d for the gaseous wall and $8*10^{-9}$ kgN/kg*d in the reactive zone behind the gaseous wall [Engelmann et al. 2004].

Problems arose with the release of additional ammonium from the cation exchange complex of the aquifers matrix. The pH was reduced because of formation of acids due to pyrite oxidation and formation of Fe(III), iron hydroxides and iron-carbon-compounds. The total change of pH over a period of one year amounts to 0.2 to 0.6 units and a further decrease is expected.

The fact that no bacteria were injected proves that bacteria are mobile and can be dormant until suitable living conditions are encountered, causing a resurrection of bacterial activity and reproduction.

The method could be applied to create desired redox conditions within the infiltration pond and the production well.

3.2 Vyredox & Nitredox [Braester & Martinell 1988]

Both processes basically consist in the re-injection of manipulated water into an aquifer with the intention to change the chemical conditions within the aquifer. In the case of Vyredox the water is aerated to increase bacterial activity and trigger the precipitation of iron and manganese. Nitredox adds the removal of nitrate and nitrite by injection of anaerobic water before the Vyredox-process. The Nitredox-process only needs to be added when there are problems with nitrate and nitrite.

Vyredox was developed in Finland in the 1960s with the first commercial application in 1969. In 1988 approx- over 100 plants worldwide operated the Vyredox- and Nitredox-Scheme.

The methods are preferred to post-production-treatment because the in-situ-treatment of polluted groundwater circumvents the problem of precipitation in the production wells as well as the creation of sludge that may have to be disposed.

The basic principle of Vyredox is the injection of aerated water into an anaerobic aquifer. The oxidation changes the redox potential within the aquifer by several hundred millivolts, creating suitable conditions for bacteria and therefore triggers bacterial activity, leading to increased natural purifying processes and to the precipitation of iron and manganese. Common water produced from the aquifer is aerated and then re-injected. There are two different types of Vyredox.

During Vyredox 1, the water is injected from the production well. This means that during injection no water for consumption is produced. The duration of the injection phase is between 20 and 30 hours. A contact time of 4 to 10 hours to form the oxidizing zone must also be added. Therefore, the plant does not produce drinking water for a period of at least 24 hours. When pumping in the production well is resumed, the hydraulic gradient causes the water to flow through the oxidizing zone to the well.

Since only a limited amount of oxygenated water is injected, the oxidizing zone decreases with time until precipitation processes finally occur close to the production well. At that point, the water production has to be ceased for another injection period.

This also means that the oxidizing zone is not steady-state but continuously moves towards and away from the production well, distributing precipitation products throughout the aquifer and limiting clogging within the pores of the aquifer.

Vyredox 2 addresses the major drawback of Vyredox 1, the non-continuous production of drinking water because of injection periods. Vyredox 2 uses an improved layout where a circle of injection wells is positioned around the production well (Figure 11). As of 1988, the number of wells in the circle ranged between 3 and 16.

The wells are operated in a pattern, independently from the production well, allowing for continuous production. In the pattern three neighbouring wells a, b and c are used simultaneously. Water is produced from wells a and c, enriched with oxygen and then re-injected in well b, located in the middle between wells a and c. This pattern is shifted along the circle of wells in time intervals, forming a superimposed hydraulic gradient to the supply well.

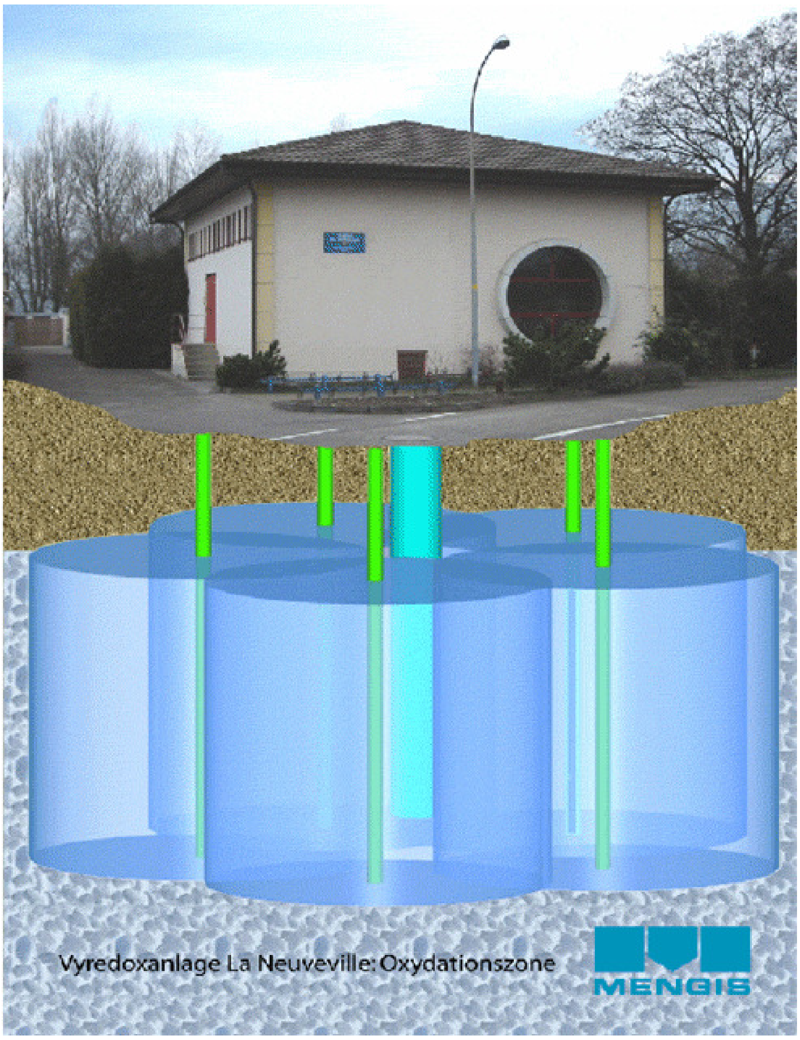

Figure 11: Oxidation zone at the Vyredox site in La Neuveville (www.mengis-gebr.ch/images/VDX_Oxy1.gif)

The Nitredox-method adds another circle of wells to the layout. In the outer ring anaerobic water in injected, creating an anaerobic, reducing zone in which nitrate and nitrite are removed by bacteria. The anaerobic water is created by mixing with an oxygen consuming substance like methanol. The inner ring represents the regular Vyredox-process, causing precipitation of iron and manganese, as well as degassing of the nitrogen-gas-products of the reducing zone. Besides an additional ring of injection wells this method requires observation wells outside of the outer ring, in between the two injection rings and in between the production well and the inner ring to monitor the in-situ-processes. Injections on the outer and inner ring are done accordingly to the principle of Vyredox 2.

All methods result in the formation of redox zonation with mobile borders, controlled by the injection rate. The main advantage of mobile borders is the distribution of precipitation products throughout the aquifer, thereby limiting clogging. A side effect is the increase of adsorption area through the precipitated solids. For iron, the transformation into more stable minerals like hematite has been observed. An efficiency rate can be defined as:

$^{\text{volume of injected water}}/_{\text{volume of produced water}}$ [Braester & Martinell 1988]

Efficiency rates range between 3 and 50 with most plants achieving a rate of 10. Results strongly depend on the fit of the oxidized zone to the aquifer and on the production well. The application of Nitredox was able to bring nitrate concentrations from over 100 mg/L down to below 25 mg/L and nitrite concentrations down to below 0.02 mg/L.

Clogging is not an issue since the pores are only affected very slowly by clogging and the mobile borders distribute precipitations throughout the aquifer. Therefore, a properly developed oxidizing zone and a plant run within specifications ensure that precipitations occur at a safe distance to the production well.

A limitation of the application of Vyredox is posed by water with very low pH-values. In this case, the groundwater usually contains methane and hydrogen sulphide, dissolved iron and manganese. The precipitation of the dissolved metals demands an increase of approx. a thousand millivolts (for manganese). Such an increase is hard to achieve. A general rule is that the lower the pH of the groundwater, the more often a re-oxygenation has to be performed.

The major problem of Vyredox and Nitredox is the high sensitivity of the methods towards the pumping regime and the fit of the reactive zones to the aquifer and the production well. The plants can only operate outside of their specifications for short periods. Water production above the capacity of the Vyredox- and/or Nitredox-layout installed will cause precipitation close to the well and reduce permeability. Increasing water demand surpassing the capacity of a plant makes the plant obsolete. Any adjustment to a higher production capacity is associated with major changes to the wells and to the well-layout.

Because the water for injection is usually derived from the aquifer the volume produced by the plant is smaller than the volume the aquifer is able to deliver and therefore inefficient.

Since the methods rely on the use of wells, common problems of well construction are an issue as well. A plant at Grimsas (Sweden) suffered from clogging of filter screens due to layers of fine material not detected during pre-construction soil sampling.

An adaptation of the Vyredox-process could be used to tune permeability of an aquifer (see chapter 2.2.5).

3.3 Deep well injection experiment [Prommer & Stuyfzand 2005]

The deep well injection experiment by Prommer and Stuyfzand [Prommer & Stuyfzand 2005] consisted of the injection of pre-treated, aerobic surface water into an anaerobic aquifer. Because the injected aquifer was situated in great depth and the water was injected instead of infiltrated, the experiment eliminated influences of the hyporheic zone, allowing a focus on the processes within the aquifer. The injection was paired with the application of a three-dimensional, reactive multicomponent transport model. The objective was to assess water quality changes during the subsurface passage, especially regarding the parameters temperature and aquifer composition.

The experiment was performed at a bank of the canal Zuid-Willemsvaart in the southern Netherlands using an injection well, a production well in 98 m distance and four observation wells. The used aquifer was made up of fine and coarse sands and covered with an aquitard of clay and loam.

The water was abstracted from the canal, pre-treated to remove heavy metals and pesticides and than injected into a depth of 300 m below ground. Deep aquifers usually contain considerable amounts of pyrite. This allowed comparing the effects of pyrite-oxidation and DOC-mineralization. The composition of the injected surface water differed clearly from the ambient groundwater (see table 6) enabling the estimation of mixing processes. The time span of the experiment was 854 days, running from July 6th 1996 to May 1999. Therefore, seasonal effects could be considered in the experiment (Table 6). The data abstracted from the injected and produced water, as well as from the four observation wells, was used in a model depicting the subsurface passage with several parameters (reactive vs. non-reactive transport, heat conductivity...).

Several conclusions were drawn from the experiment:

Pyrite oxidation accounts for a large fraction of the removal of oxygen and nitrate, is a main driver for water quality changes and varies strongly with temperature of the injected water and presence of bulk organic material in the aquifer (competition for being the reductants).

Table 7: Water properties during deep well injection experiment [after Prommer & Stuyfzand 2005]

	ambient groundwater	injectant range	injectant winter	injectant summer
ph	6.68	6.75 – 7.35	7.1	6.9
trace elements [mol/L]	10^{-4}	10^{-3}	10^{-3}	10^{-3}
oxygen [mol/L]	0	$3.5 – 8.13 \times 10^{-4}$	8.13×10^{-4}	3.60×10^{-4}
Nitrate [mol/L]	0	$2.42 – 5.48 \times 10^{-4}$	3.54×10^{-4}	2.42×10^{-4}
Fe(II) [mol/L]	10^{-4}	0	0	0
Fe(III) [mol/L]	10^{-12}	10^{-8}	10^{-7}	10^{-7}
DOC [mol/L]	0	10^{-4}	10^{-4}	10^{-4}
temp [°C]	17	1.9 – 22.8	1.9	21.5

Reaction rates depended significantly on temperature. The highest concentrations of oxygen (first component to be reduced and therefore a prime indicator for redox processes) corresponded to the lowest temperatures of the injected water while no oxygen was detected (at all observation wells) for temperatures above 14°C. A similar pattern was detected for nitrate (second component to be reduced once oxygen is depleted) which was completely removed for some short periods, when the temperature of the injectant was the highest, in contrast to little to no removal for the winter period when temperatures where low. The experiment therefore revealed **14°C to be a critical temperature** at which bacterial activity is significantly decreased.

The competition between organic compounds (bulk organic matter BOM, dissolved organic carbon DOC) and pyrite as reducing agents was quantified. A total oxidation capacity of 9.11×10^6 mol electron equivalent (= mol eeq) was injected during the experiments. It was calculated that pyrite oxidation consumed 6.34×10^6 mol of the added oxidation capacity compared to 1.64×10^6 mol eeq consumed by mineralization of BOM.

Observation of the breakthrough of water quality changes lead to the conclusion of significant dispersion caused by a broad spectrum of travel times between injection and extraction well. It was concluded that dispersion of the flow field leads to almost complete dissipation of seasonal variations with regard to water quality and temperature dependent reactivity.

In conclusion: The experiment was able to examine effects of temperature and aquifer composition because the "injection" approach circumvented the highly reactive hyporheic zone while the depth of the aquifer excluded effects of re-oxidation. The chosen method of analysis did not permit a differentiation of temperature dependencies of pyrite oxidation and DOC mineralization.

The findings concerning temperature were confirmed by several investigations conducted at the AR-site at Lake Tegel Berlin where seasonal temperature changes showed strong influence on the chemistry of groundwater [Greskowiak et al. 2005].

Chapter 4
Summary and conclusions

During artificial recharge of groundwater redox reactions and the resulting redox zonation play a decisive role in determining the water quality of the produced water. A classification following McMahon & Chapelle [2008] is best suited to describe redox zonation in AR systems: oxic zone (presence of O_2), sub-oxic zone (no oxygen but nitrate present) and anoxic zone (Fe- and Mn reducing zones).

The optimal redox zonation for maximum removal of redox-dependent substances or substance groups should be determined based on the contaminants present in the source water. However, there are some general statements that can be made:

- Anoxic to anaerobic conditions are of benefit only if certain substances or substance groups need to be removed during subsurface passage (nitrate, most desinfection-byproducts (THMs), some pesticides (triazines), some pharmaceuticals and x-ray-contrast media (sulfamethoxazole, carbamazipine, AOI) or highly soluble chlorinated hydrocarbons (e.g. PCE)). If these substances are not present in the source water (at relevant concentrations) anoxic to anaerobic conditions should be avoided in order not to mobilize iron and manganese (and other related inorganic trace elements).
- Maximum benefit for oxic to suboxic subsurface passage is reached after 30 d, for anoxic to anaerobic subsurface passage after 100 d.
- 15 d of oxic / suboxic and 2 d of anoxic / anaerobic passage already lead to substantial removal or redox-sensitive substances or substance groups. A minimum of 5 d for oxic / suboxic subsurface passage is recommended in order to achieve a relevant effect for most of the regarded substances or substance groups.

The main drivers for redox zonation in AR systems are:

- Availability of oxidizing agents (oxygen, nitrate), influenced by aquifer geochemistry (organic matter, mineral phases), temperature, natural gw recharge, presence & thickness of unsaturated zone, water table oscillations
- Availability of reducing agents (organic matter, reduced mineral phases), influenced by geochemistry of infiltration basin material, aquifer geochemistry, mixing with ambient groundwater
- Biological activity (in infiltration pond and subsurface), influenced by temperature, nutrient availability and for infiltration ponds additionally sunlight.

- Residence time, influenced by well field geometry, distance pond to production well, pumping rate, hydraulic conductivity of aquifer and clogging layer, presence & thickness of unsaturated zone, temperature (water viscosity), retardation coefficient

Possibilities for manipulation exist in different elements of the AR system:

- Infiltration pond (e.g. controlled algal growth to decrease DOC, control sunlight and temperature, water movement, addition / avoidance of nutrients)
- Hyporheic zone (e.g. control temperature, use of specific filter material with defined org. C or high adsorption capacity, control infiltration rates to enhance formation of unsaturated zone)
- Subsurface passage (e.g. application of redox controlling substances via injection wells, controlling residence times by adjusting pumping rates or creating hydraulic barrier, wells at different distances from infiltration pond, manipulating hydraulic conductivities through precipitation)

For newly constructed AR systems the well field design could be optimized with respect to redox zonation, as long as other requirements are met.

Two examples of redox control measures (for artificial re-oxidation of a polluted aquifer “BIOXWAND®” on the one hand, and injection of treated water to enhance the redox conditions in the aquifer “Vyridox” and “Nitridox” on the other hand) provide concrete application of redox control during Aquifer Recharge. For redox control in AR ponds, however, no practical application was found.

This report is the basis for a study to be conducted within the following months to develop recommendations for practical implementation of redox control schemes in AR ponds and preceding pilot scale experiments.

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Appendix A

Detailed Description of the Different Elements of an AR System

The Infiltration Pond

An infiltration pond is basically a regular pond, usually located next to a production well. Infiltration of water raises the water table beneath the pond while the production well creates a cone of depression. Both changes of the water table in combination form a hydraulic gradient and therefore control flow velocity, residence time and flow paths within the subsurface.

A common phenomenon during pond infiltration is the development of a clogging layer. This results from enhanced biological activity (see chapter 1.2) in the uppermost centimeters of the sediment and accumulation of fine materials in the pores, causing a reduction of permeability. Mechanisms for clogging of the interstices may be biological (growth of biofilm), physical (input of fine sediments, build-up of gas bubbles) or chemical (precipitation of mainly carbonates) [Gunkel & Hoffmann 2009]. The clogging layer is the reason why infiltration ponds are often run in operational cycles [Massmann et al 2006a].

For the AR site at Lake Tegel, Massmann et al. (2006a) describe the operational cycle as follows:

The operational cycle begins with a re-development of the pond once permeability has been permanently reduced below acceptable values by the formation of a clogging layer. Water supply is interrupted and no more water is discharged into the pond, leaving the remaining water in the pond to infiltrate. Once all water has infiltrated the uppermost layer of pond sediment is removed or cleaned, thereby basically removing the clogging layer and restoring permeability. In Berlin, the sand is washed in order to remove the accumulated fines and then re-applied to the pond. The success of re-development is variable. Data from Massmann et al (2006a) shows that the maximum value of the infiltration rate after re-development can be up to five times the original value but this state is not reached for every re-development [Massmann et al 2006a, figure 4]. The same paper gave the range for the lifetime of a re-development between one and four months. Possible reasons for these variations are variations in source water quality, high heterogeneity of sediments or (seasonal) varying levels of clogging intensity. Reactions of the clogging layer with oxygen from the atmosphere during re-development may also influence the permeability [Massmann et al 2006a, figure 3].

After re-development the pond is refilled with (surface) water. Usually the water level is kept constant (water level determines the hydraulic pressure, therefore a constant water level causes a constant hydraulic pressure [Gunkel & Hoffmann 2009]). The water infiltrates into the subsurface through the banks and bottom of the infiltration pond. From there the water spreads away from the pond radial in all directions. With the progress of time conditions between the pond bottom and the water table change from unsaturated or partly saturated to saturated. Meanwhile, the water table is elevated in the surroundings of the infiltration pond. In addition, the processes that form the clogging layer commence.

A third stage is reached when, due to the clogging, permeability is (significantly) reduced. Saturation decreases correspondingly which further decreases permeability. At some point, when permeability has dropped below acceptable values, re-development is performed again, restarting the operation cycle (at the AR-Site Lake Tegel in Berlin re-development is performed once infiltration rates reach 1 m/d [Massmann et al 2006a, figure 4]).

While the formation of a clogging layer reduces the performance of AR-system with respect to water flow, there are also benefits. Reduced permeability yields longer travel times of the water and therefore a longer time period for chemical reactions and biochemical degradation. The clogging layer itself contributes to the improvement of water quality. The organic and fine-grained materials increase capacities for adsorption and reduction [Massmann et al 2007b].

The Hyporheic Zone

The hyporheic zone is defined as the interface between surface water and groundwater [Gunkel & Hoffmann 2009] and therefore describes the zone between the pond base and the groundwater. The name is derived from the greek words hypo, meaning “below”, and rheos, meaning "flow" [Orghidan, 1959]. Several studies show that the most significant chemical changes occur within the first meters of infiltration, in the hyporheic zone ([Hoehn et al 1983], [Jacobs et al 1988], [Doussan et al 1997], [Brugger et al 2001]). This has been attributed to the fact that these sediments are very reactive environments and the highest microbial activity is located within them [Jacobs et al 1988, Doussan et al 1997, Brugger et al 2001 cited after Massmann et al 2008, Hiscock & Grischek 2002 cited after Massmann et al 2007b].

Conditions within the hyporheic zone may be saturated or unsaturated. In the latter case we speak of the existence of a vadose zone. The pores within the vadose zone contain water and air while the pressure head is below atmospheric pressure, and water is retained by adhesion (funiculary groundwater) or capillary action (capillary groundwater).

The thickness of the vadose zone ranges between a few centimeters and over a hundred meters. Generally, its thickness is greater in arid areas.

The vadose zone has a strong filter-effect for microorganisms due to its partial saturation since only thin films of water are in the pores and limit the transport capacity of microorganisms with and within the water. Additionally, microorganisms may be adsorbed on the sediment surface. For this reason, infiltration ponds for drinking water production in France are required to show unsaturated conditions below the pond.

In infiltration ponds an artificial layer of sand with a thickness of approx. 0.5 to 1.0 m is usually applied if no natural sandy layers exist [Balke et al 2000, p.525]. The German DVGW guidelines [DVGW 2007] give recommendations to introduce a 0.2 to 5 m thick filter sand layer with grain sizes between 0.1 mm and 3 mm, depending on the desired infiltration velocity, the hydraulic conductivity of the aquifer and the quality of the infiltrating water. In addition a supporting layer of 10 cm thickness is recommended as basis with 3-fold grain diameter of the filter sand.

The Subsurface Passage

The subsurface passage is defined as the zone between the groundwater surface and the production well. As oxygen input is limited, subsurface passage often exhibits anoxic to anaerobic conditions. The subsurface passage functions as hydrogeochemical system/environment for processes like mixing, adsorption, precipitation and slower biodegradation. With regard to water treatment the main benefits of the subsurface passage are the removal of nitrate and of trace organic compounds from source water that are predominantly removed under anoxic to anaerobic conditions.

The system “subsurface passage” is an open system. Ambient groundwater may enter from the sides and from below, leading to dilution. AR is commonly practiced within sedimentary aquifers. Therefore, superposing layers of the aquifer are permeable and form an unsaturated zone. Through this unsaturated zone, input into the system is possible, e.g. rainwater or gaseous oxygen may intrude. Changes of the water table may trap gas in the pores. Input of oxygen may result in a re-oxidation. This should be desirable since it causes precipitation before the actual well is reached. It could avoid a reduction of permeability through precipitation in the well and thereby increasing the lifespan of the well.

The Production Well

The production well consists of the well interior, the tubing and the gravel pack. The well promotes re-oxidation (e.g. by mixing water from different depths) along with precipitation of trace elements like iron or manganese. The latter may reduce the production capacity of the well. Avoidance of mobilization of trace elements or their precipitation far away from the well is a highly desired objective (the avoidance should be favoured in order not to clog pore space with precipitates).

Appendix B

Micro-organisms in the subsurface

Soil and groundwater are habitats for microorganisms consisting of one or several cells. The abundance of autochthonous microorganisms decreases with depth and levels at a density of approx. 10^4 cells/1g of sediment [Griebel & Mösslacher 2003]. These organisms use contents of the water for their metabolism and dispense products of their metabolism into the groundwater (= microbial catalysed metabolism). There is a substantial interaction between microbial activity and redox conditions. While micro-organisms may not change the direction of a reaction, they influence its kinetics [Hem 1961, cited after Mattheß 1994].

Within the shallow groundwater, the microbial population consists of bacteria, archaea, protozea and funguae. Within the deeper groundwater, only bacteria and archaea are encountered [Griebel & Mösslacher 2003, p.91]. The composition of the population of microorganisms is controlled by ecological factors [Scheffer & Schachtschabel 1982, cited after Mattheß 1994], [Griebler & Mösslacher 2003, p.54]:

- oxygen content
- water saturation
- temperature (present day estimate: max. temperature that allows life, i.e. approx. 120°C)
- availability of nutrients (N, P, DOC, bound sulfuric compounds)
- chemical environment (pH, E_H, Total Dissolved Solids (TDS))

The presence of oxygen is the most important environment parameter since microorganisms are divided into aerobic, facultative anaerobic and obligate anaerobic populations. Oxygen is toxic for the latter group. Some bacteria may use oxygen bound in molecules instead of free oxygen, especially nitrate and sulfate [Mattheß 1994].

Even though many bacteria are able to move actively within the water, approx. 80% of all bacteria live stationary, attached to solid particles [Wolters & Schwarz 1956 cited after Mattheß 1994]. The accumulation of bacteria on the surface leads to the formation of biofilms consisting of: aggregations of bacteria, a matrix made from polysaccharides, organic and inorganic compounds and entrapments, enzymes and water. In groundwater environments biofilm thickness is usually limited to only a few layers of cells [Griebler & Mösslacher 2003, p.121]. An important aspect of biofilms is that several kinds of bacteria exist in close neighbourhood and together are able to process even complex compounds.

The population density of bacteria is correlated to the supply with nutrients and the removal of harmful metabolic products. Therefore, a higher flow velocity yields a denser population [Schmidt 1963, cited after Mattheß 1994]. The main nutrients for microbial populations are compounds containing nitrogen (ammonia, organic nitrogen compounds) and phosphate. In the anoxic and anaerobic zone all compounds carrying oxygen, especially nitrate and sulphate, serve as nutrients.

Table 8 gives an overview of population densities typically encountered in different environmental compartments. At Lake Tegel in Berlin a maximum concentration of 2 x 10^9 cells/1 gram sediment were found within depths of 0 to 0.5 cm, decreasing to 0.2 x 10^9 cells/ 1 gram sediment in depths > 20 cm [Spring et al 2000, Emtiazi et al 2000, all cited after Gunkel & Hoffmann 2009].

Table 8: Population densities of micro-organisms in the environment [Griebel & Mösslacher 2003].

Environment	**Population density**
surface water	10^5 to 10^{11} cells per liter
groundwater	10^6 to 10^9 cells per liter
top-soil	up to $25*10^9$ cells per gram
deep aquifer	10^3 cells per gram

Appendix C

Hydro- and Geochemical Processes that lead to Redox Zonation

The following description gives an overview of the processes occurring along the redox zonation when a sedimentary aquifer is infiltrated by a surface water of common constitution with oxygen, nitrate, sulfate and organic compounds solved in the water.

1) Oxygen reduction

The first component to be reduced is oxygen because it yields the highest reduction of Gibbs free energy for the system and is able to react with (almost) every other chemical substance. Reduction of oxygen is primarily coupled with oxidation of organic materials as well as the oxidation of sulfur-bearing minerals commonly referred to as pyrite oxidation. The general redox-reaction of oxygen and organic material is given in the following equation:

$$CH_2O + O_2 \Rightarrow CO_2 + H_2O \qquad (3)$$

It should be noted that oxidized organic materials can be much more complex than stated in equation 3. Besides organic matter/particulate organic carbon (POC) in the subsurface, for example peat, dissolved organic carbon (DOC) leached from the upper soil can take part in the reaction. The reaction yields carbon dioxide, which can influence the $CaCO_3$-CO_2-equilibrium and result in a decrease of pH and a dissolution of carbonatic materials [Thorstenson et al. 1979, Chapelle et al. 1987 cited after Apello & Postma 1996].

The penetration depth of dissolved oxygen depends on the amount of reductants encountered and on the interaction between flow velocity and reaction kinetics. Infiltration through a soil with high C_{org}-concentrations can rapidly remove oxygen. The range of O_2-reduction is exemplified by the following data:

- complete depletion of all oxygen within 0.5 m depth (infiltration pond in Berlin) [Greskowiak et al. 2005, p.6]
- oxygen found in depths of up to 8000 m in relation with diagenesis [Fairbridge 1967, cited after Mattheß 1994, p.157]
- oxygen found in depths between 100 and 1000 m in aquifers in Nevada, Arizona, Arkansas and hot springs of the folded Appalachians, water ages up to 10.000 years and a travel distance from point of recharge of approx. 80 km [Winograd & Robertson 1982]

2) Nitrate reduction

The reduction of nitrate to N_2 creates several intermediates (NO_2^-, NO and N_2O, see equation 4) which may cause a sensitivity of reaction kinetics towards chemical conditions (e.g. which pH is encountered) because of the necessary transfer of electrons and other elements like hydrogen. Nitrate reduction is the only means for nitrate removal within aquifers [Apello & Postma 1996].

$$\underset{+5}{NO_3^{1-}} \overset{0.775V}{\Rightarrow} \underset{+4}{NO_2} \overset{1.093V}{\Rightarrow} \underset{+3}{HNO_2} \overset{0.996V}{\Rightarrow} \underset{+2}{NO} \overset{1.59V}{\Rightarrow} \underset{+1}{N_2O} \overset{1.77V}{\Rightarrow} \underset{0}{N_2} \overset{0.275V}{\Rightarrow} \underset{-3}{NH_4^{1+}}$$

(4)

Only a small amount of solved nitrate is reduced through oxidation of dissolved reduced species in the groundwater, since the concentration of nitrate exceeds concentrations of reducing species. The major removal of nitrate is due to pairing with the oxidation of organic matter, commonly referred to as "denitrification", exemplified with the following equation:

$$5\ CH_2O + 4\ NO_3^- \Rightarrow 2N_2 + 4HCO_3^- + CO_2 + 3H_2O \qquad (5)$$

Besides organic matter present in the subsurface, remaining dissolved organic carbon (DOC) leached from soils is part of the redox-reaction with nitrate [Starr 1988, Starr & Gillham 1989]. Reduction of nitrate is mainly controlled by the reactivity of organic matter. It should be noted that reduction of nitrate and therefore its removal is highly desired with regard to drinkiing water production, while reduction of oxygen seems to be an unavoidable process during infiltration that has to be reversed upon production through aeration.

Since organic matter is rarely the main constituent of an aquifer, redox-reactions coupling reduction of oxygen and nitrate with oxidation of minerals forming the aquifer's matrix must be considered. An exemplary reaction is the pyrite-oxidation.

1) through oxygen (rarely occuring under saturated conditions):

oxidation of polysulfides S_2^{2-} : $FeS_2 + {}^1/_2\ O_2 + H_2O \Rightarrow Fe^{2+} + 2\ SO_4^{2-} + 2\ H^{1+}$ (6)

oxidation of Fe^{2+} to Fe^{3+}: $Fe^{2+} + ¼\ O_2 + H^{1+} \Rightarrow Fe^{3+} + ½\ H_2O$ (7)

=> $FeS_2 + {}^{15}/_4\ O_2 + {}^7/_2\ H_2O \Rightarrow Fe(OH)_3 + 2\ SO_4^{2-} + 4H^+ = Fe(OH)_2 + 2H_2SO_4$ (8)

2) through nitrate

$2FeS_2 + 6NO_3^- + 2H_2O \Rightarrow 3N_2 + 2FeOOH + 4SO_4^{2-} + 2H^+$ (9)

Oxidation of pyrite by nitrate only occurs once (all) oxygen is consumed. The many intermediates appearing during pyrite oxidation indicate complex reaction mechanisms. An increased sensitivity towards chemical conditions can be expected. For example the pH controls which intermediates are created during oxidation of polysulfides as well as the reaction rate for the oxidation of Fe^{2+} [Apello & Postma 1996].

Shortage of oxidants significantly weakens the oxidation of Fe^{2+} to Fe^{3+}. Precipitation of Fe^{3+} (for example as FeOOH) can hinder further oxidation of Fe^{2+} by creating a protective layer on the pyrite, any further oxidation of Fe^{2+} then depends on diffusion through that layer [Nichelson et al 1990].

3) Iron-reduction

Further shortage of oxidants causes an increase of dissolved iron (Fe^{2+}) in the water. Manganese, possessing similar chemical properties like iron and also present in aquifers, becomes dissolved as well. With respect to the production of drinking water, there are several drawbacks to the mobilization (e.g. solution) of iron and manganese into the water. Precipitation of iron within the aquifer may theoretically lead to clogging and therefore reduction of permeability (apparently not observed in practice so far). A more serious problem is the precipitation of iron- and manganese-compounds upon production of the water. Contact with the atmosphere leads to solution of oxygen which binds with iron and manganese to oxides in the form of suspended solids. Apart from clogging water lines through precipitation the suspended solids give the water unacceptable taste, odour and appearance (with regard to drinking water) and need to be removed by adapted post-treatment.

4) Sulfate reduction

With oxygen and nitrate reduced, sulfate SO_4^{2-} becomes the next preferred oxidant for oxidation of organic matter. The reduction is catalysed by bacteria and described by:

$2\ CH_2O + H_2SO_4 = HS^{1-} + H_2O + CO_2$ [Champ et al 1979, Stumm & Morgan 1981] (10)

Sulfate-reduction forms the toxic compound hydrogen sulfide H_2S. Larger amounts of dissolved hydrogen sulfide bind with Fe^{3+} (respectively compounds containing Fe^{3+}, for example FeOOH) over intermediates to pyrite FeS_2 and precipitate. This process is referred to as pyrite-reduction (and produces hydrogen H_2). Therefore, the sulfidic zone is characterized by the absence of dissolved iron.

The methanic zone is the final stage of redox zoning. Organic matter is reduced to methane by the hydrogen produced during the precipitation of pyrite. This reaction is paired with the oxidation of carbon dioxide:

$$CO_2 + 4H_2 \Rightarrow 2\ H_2O + CH_4 \qquad (11)$$

Because oxidation of methane can be used as a source of energy for the reduction of sulfate, the border between the sulfidic and the methanic zone is rather distinct [Iversen & Jørgensen 1985]. Low concentrations of sulfate therefore indicate the methanic zone. Fermentation of organic compounds is also occurring:

$CH_3COOH \Rightarrow CH_4 + CO_2$ [Vogels et al 1988, cited after Apello & Postma 1996](12)

In addition, iron becomes mobilized once again from the aquifer material.

Instead of directly measuring the redox potential (which will be a mixing potential), redox zones are commonly identified by the disappearance of oxygen, nitrate and sulfate as well as the appearance of manganese and iron. Table 2 lists the important redox reactions commonly occurring during artificial recharge, giving the oxidizing and reducing agents as well as the energy yield.

Appendix D

Redox-dependent removal during subsurface passage of substance groups relevant for drinking water treatment

	no information on redox dependency available	no redox dependency	any change of redox zonation may influence mobility	enhanced removal under oxic conditions	enhanced removal under anoxic/ anaerobic conditions
Particles and particle-bound substances					
TSS		x			
Pathogens	x			(x)	
Cyanotoxins	(x)			x	
Main water constituents					
Nitrate					x
Ammonium				x	
TDS		x			
DOC				x	
Trace substances					
DBPs					
THMs					x
Pesticides					
organochl. insecticides, anilines		x			
ureas, phenoxy herbicides				x	
triazines					x
PhACs					
chlarithromycine, dehydroerithromycine, toxithromycine, trimethoprime		x			
sulfadiazine, bezafibrate, indometacine, diatrizoic acid, PDP	x				
clofibric acid, primidone		x			
clindamycine, phenazone, propyphenazone, diclofenac, iopromide, AAA, AMDOPH, AMPH, DP, FAA				x	
sulfamethoxazole, carbamazipine, AOI					x
Chlorinated hydrocarbons					
less soluble CHCs		x			
highly soluble CHCs (PCE)					x

	no information on redox dependency available	no redox dependency	any change of redox zonation may influence mobility	enhanced removal under oxic conditions	enhanced removal under anoxic/ anaerobic conditions
Cyclic aromatic hydrocarbons					
monocyclic aromatic hydrocarbons		x			
PAKs		x			
EDCs	x				
Other trace organics					
1,5-NDSA, NPS, EDTA, MTBE		x			
1,7-NDSA, 2,7-NDSA				x	
Inorganic trace elements			x	(x)	

Appendix E

Overview of common components within surface water and their removal during subsurface passage [Grützmacher et al in prep.]

group	examples	removal	redox sensitive
suspended solids		high	no
pathogens	bacteria, viruses, protozea	high	(no)
cyanobacterial toxins	algae	high	yes
nitrate	nitrate NH_3	high	yes
desinfections by-products (DBP)	Trihalogenmethanes (THM): Hydrates , Cyanogene, Chlorides , bromates Haloacetontriles (HAN) halogenated acetic acids (HAA)	high	yes (slightly)
(bulk) DOC = dissolved organic carbon		variable	yes (median)
Pesticides	Triazines , Ureas , Phenoxy herbicides (Mecopropp MCPP) organochloride insecticides	variable max. 50%	yes (substance- dependent)
Pharmaceutical active compounds (PhACs)	- Antibiotics (Clarithromycin , D-Erythromycin , Roxithromycin , Sulfamethoxazole (SMOX) Trimethophrin) - lipid regulators (Bezafibrate , clofibric acid) - Anticonvulsants (carbamazepine , primidone) anti inflamory drugs (phenazone , propyphenazone ,diclofenac , indometacine)	variable	yes (strong)
x-ray-contrast media (x-cons)	AOI (sum parameter) , Iopromide		
Transformation products PhACs &xcons	AAA , AMDOPH , AMPH , DP , FAA		
chlorinated halogens (CHC)	Dichlorethane (DCA) , Trichlorethane (TCA) , Tetrachlorethylene (PCE) , Carbon Tetrachloride (CTC)	variable	yes
mono- and polycyclic hydrocarbons	monocyclcit aromatic hydrocarbons (BTEX) polycyclic aromatic hydrocarbons (PAH)		
other organic trace compounds	NDSA , EDTA , MTBE , NPS	variable	yes (slightly)
Ammonium	NH_4	none (remobil.)	yes (strong)
major cations & anions Total dissolved solids TDS	cations: Mg^{2+}, Na^+ , K^+ anions: SO_4^{2-} , Cl^- , Cl^- , HCO_3^-	none (demobil.)	no (minor)
inorganic trace elements	from anthropogenic activity: Pb, Cu, Zn, Cd from subsurface material: As, F, Fe, Mn, Se, Cr, U	none (demobil)	yes (strong)