

WP5.2: Combination of MAR and adjusted conventional treatment processes for an Integrated Water Resources Management

Deliverable 5.2.9

Relevance and opportunities of bank filtration to provide safe water for developing and newly industrialised countries



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Introduction

Bank filtration (BF) denotes the process whereby river water is induced to infiltrate into a groundwater system by well operation adjacent to banks. In Central Europe, BF has been common practice for 100 years to produce drinking water. Due to the easy implementation and little maintenance necessary, BF has been suggested to be a useful drinking water treatment for developing and newly-industrialised countries. Experience from Europe has demonstrated that BF is suitable to remove a range of organic and inorganic contaminants while an exhaustion of cleaning capacity has not been observed. BF systems can mitigate shock loads and are particularly known for the efficient removal of pathogens, suspended solids and toxic algae from surface water, all being water quality parameters of high relevance in developing and newly-industrialised countries. Another benefit of BF operation is the storage capacity which may help to balance freshwater availability in areas experiencing high variations of precipitation and run-off. This report aims at evaluating the relevance and opportunities of BF systems to provide safe water to these countries.

Approach

In order to evaluate the relevance and opportunities of BF systems to developing and newly-industrialised countries, the report is structured to address key considerations and

- (i) identify prerequisites for successful BF operation based on the experience in Central Europe and the United States,
- (ii) assess the removal potential of BF for various water contaminants based on available literature, the TECHNEAU investigations in India and NASRI data from Berlin,
- (iii) evaluate the sustainability and relevance of BF operation with regard to the particular needs in developing and newly-industrialised countries.

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TKI Categorisation

Classification							
Supply Chain		Process Chain		Process Chain (cont'd)		Water Quality	Water Quantity (cont'd)
Source		Raw water storage		Sludge treatment		Legislation/regulation	- Leakage
- Catchment		- Supply reservoir		- Settlement		- Raw water (source)	- Recycle
- Groundwater	X	- Bankside storage	X	- Thickening		- Treated water	
- Surface water	X	Pretreatment		- Dewatering		Chemical	
- Spring water		- Screening		- Disposal		- Organic compounds	X
- Storm water	X	- Microstraining		Chemical dosing		- Inorganic compounds	X
- Brackish/seawater		Primary treatment		- pH adjustment		- Disinfection by-products	X
- Wastewater		- Sedimentation		- Coagulant		- Corrosion	
Raw water storage		- Rapid filtration		- Polyelectrolyte		- Scaling	
- Supply reservoir		- Slow sand filtration		- Disinfectant		- Chlorine decay	
- Bankside storage	X	- Bank filtration	X	- Lead/plumbosolvency		Microbiological	
Water treatment		- Dune infiltration		Control/instrumentation		- Viruses	X
- Pretreatment		Secondary treatment		- Flow		- Parasites	X
- Primary treatment	X	- Coagulation/flocculation		- Pressure		- Bacteria	X
- Secondary treatment		- Sedimentation		- pH		- Fungi	- In water safety/quality
- Sludge treatment		- Filtration		- Chlorine		Aesthetic	- In security of supply
Treated water storage		- Dissolved air flotation		- Dosing		- Hardness / alkalinity	X
- Service reservoir		- Ion exchange		- Telemetry		- pH	X
Distribution		- Membrane treatment		Analysis		- Turbidity	X
- Pumps		- Adsorption		- Chemical		- Colour	X
- Supply pipe / main		- Disinfection		- Microbiological		- Taste	X
Tap (Customer)		- Dechlorination		- Physical		- Odour	X
- Supply (service) pipe		Treated water storage					- For infrastructure
Internal plumbing		- Service reservoir				Water Quantity	- For security of supply
							Risk Communication

- Internal storage		Distribution					- Communication strategies	
		- Disinfection				Source	- Potential pitfalls	
		- Lead/plumbosolvency				- Source management	- Proven techniques	X
		- Manganese control				- Alternative source(s)		X
		- Biofilm control				Management		
		Tap (Customer)				- Water balance		
		- Point-of-entry (POE)				- Demand/supply trend(s)		
		- Point-of-use (POU)				- Demand reduction		

TKI Categorisation (continued)

Contains		Constraints		Meta data				
Report	x	Low cost	x	<i>Iris Huelshoff, Janek Greskowiak, Bernd Wiese & Gesche Grützmacher</i>				
Database		Simple technology	x	<i>KompetenzZentrum Wasser Berlin</i>				
Spreadsheet		No/low skill requirement	x	<i>Iris Huelshoff</i>				
Model		No/low energy requirement	x	<i>iris.huelshoff@kompetenz-wasser.de</i>				
Research		No/low chemical requirement	x					
Literature review	x	No/low sludge production	x	<i>SINTEF</i>				
Trend analysis		Rural location						
Case study / demonstration		Developing world location	x					
Financial / organisational								
Methodology								
Legislation / regulation								

Colophon

Title

Relevance and opportunities of BF to provide safe water for developing and newly-industrialised countries

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Glossary

Ambient groundwater	synonymous with natural, landside-, inland-, background groundwater
Bank filtration (BF)	the infiltration of a river into a groundwater system induced by water abstraction adjacent to banks
Decay	either the die-off of microorganisms or radioactive decay
Heavy metals	varying definitions by toxicity or density ($>4.5 \text{ g/cm}^3$) exist. The term herein summarises for simplicity inorganic trace pollutants including heavy metals, semi-metals and one halogen (fluoride) problematic to groundwater systems
Ion exchange	exchange between different ions and a matrix. In aquifers: mainly cation exchange
Managed Aquifer Recharge	umbrella term for different aquifer recharge techniques (e.g. via infiltration ponds, bank filtration, aquifer storage and recovery, ASR)
Removal	herein used synonymously with reduction, refers to all processes which cause a decrease in concentration after subsurface passage except mixing
Retention time	synonymous to residence time, travel time
Source water	river or lake water used for drinking water production

1 Introduction

The work package WP 5.2 “Combination of Managed Aquifer Recharge (MAR) and adjusted conventional treatment processes for an Integrated Water Resources Management” within the European Project TECHNEAU (“Technology enabled universal access to safe water”) investigates river bank filtration (BF) + post-treatment as a MAR technique to provide sustainable and safe drinking water supply to developing and newly industrialised countries. One of the targets of WP5.2 is to analyse the relevance and opportunities of BF for drinking water supply in those countries.

In general, MAR is used to (i) enhance the quality of treated sewage and surface water for both potable and non-potable use and (ii) prevent overuse of aquifers, saltwater intrusion and land subsidence. Common MAR techniques include BF, basin aquifer recharge (BAR) and aquifer storage and recovery via injection wells (ASR).

Bank filtration (BF) is the abstraction of water from aquifers that are hydraulically connected to a surface water body which is in most cases a riverine system. By pumping from wells adjacent to a river or lake, the groundwater table is lowered and the surface water infiltrates into the aquifer. This so-called bank filtrate moves towards the production wells where it mixes with the ambient groundwater originating from the land side. BF has been common practice in many European cities for more than 100 years and was originally initiated to remove pathogens and suspended solids from increasingly polluted surface waters. For drinking water production, BF is regarded as a pre-treatment step in the overall treatment chain, since not all undesired substances can be removed during aquifer passage. Depending on the quality of the extracted raw water, treatment techniques that follow BF may include oxidation/ozonation, sand filtration, activated carbon filtration and safety disinfection (Schmidt *et al.*, 2003). BF as pre-treatment for nanofiltration has been reported to be even more effective for reduction of membrane fouling than microfiltration (Speth *et al.*, 2002).

Despite its long history in Europe, BF is not very common in developing and newly-industrialised countries (TZW, 2006a). In these countries, drinking water production relies mainly on the direct use of surface water and groundwater abstraction. Mismanagement and pollution, as well as growing competition for the use of water resources, has worsened the situation and led to quality deterioration. On-going, explosive urbanisation and the rise of megacities constitute new challenges to water suppliers. By the year 2010, more than half of the world’s population is expected to live in cities (IHP, 2006). In many countries, especially in warm and dry climate zones, these developments will result in strong depletion and contamination of freshwater resources. In large regions of Southeast Asia, for example, a groundwater boom over the last decades has triggered the decline in groundwater levels. Wells are running dry, energy and pumping costs increase, drought protection is minimised. Land subsidence, salinisation and health hazards are the result, the latter due to the mobilisation of toxins (Sharma *et al.*, 2006). In

this context, BF may give relief by replenishing the stressed groundwater resources with surface water which, in addition, becomes filtered during subsurface passage.

Usually, BF is relatively easy to integrate with existing technology and easy to operate requiring little maintenance (Partinoudi & Collins, 2007). However, prior to the design of a BF system, hydrogeological investigations are necessary. From the few studies available, there is also indication that BF is a cost efficient pre-treatment step. The present report is aimed at

- (i) assessing the removal potential of BF for various water contaminants
- (ii) identifying the prerequisites for successful BF operation
- (iii) evaluating the sustainability and relevance of BF systems for developing and newly-industrialised countries,

This report is meant to provide an overview of the opportunities that BF provides for developing and newly-industrialised countries. The herein compiled information is to support these countries in the evaluation whether BF may constitute an attractive supplement or even an alternative to their water supply system.

Chapter 2 (“Hydrological requirements and elimination potential of BF”) covers prerequisites and hydrological requirements for BF as well as the elimination potential for a range of water quality parameters. The subchapters shall provide general information on the respective water pollutants and reflect our current knowledge on their fate during subsurface passage and bank filtration. Each subchapter is preceded by a box highlighting the key findings since the subchapters may be too detailed for the quick reader. For a quick and informative overview on relevance and removal potential of BF in developing and newly-industrialised countries, the reader is directly referred to Chapter 3 (“The potential of BF for developing and newly industrialised countries”).

2 Hydrological requirements and elimination potential of BF

2.1 Hydrological requirements

- Developing and newly-industrialised countries are particularly affected by water shortages. BF is deemed useful in such regions to manage variations in freshwater availability but experience is yet scarce
- Prerequisite for successful BF operation is the availability and sustainable use of surface- and groundwater resources
- Hydraulic conductivities of $k_f > 10^{-4}$ m/s, a minimal thickness of 5 m and good hydraulic connection to the adjacent surface water are favourable conditions for BF
- BF offers storage capacity for regions of seasonal variations in precipitation and run-off regimes (e.g. monsoon, floods, droughts)

For the operation of a BF system, some basic requirements are mandatory. The **availability of surface water** as the primary source is the most essential parameter for a BF plant. A second major consideration is that during operation, **groundwater levels** in the surroundings of the BF well field should not decline below an ecologically and economically justifiable threshold value. It should be ensured that water abstraction does not result in adverse effects to the aquifer (overexploitation, damage to ecosystems) or the river downstream the BF site (e.g. dependent settlements being water-deprived). Other factors to be considered for successful BF operation comprise **soil texture** as well as **water and soil quality**. The soil texture should exhibit filter properties. Limestone and dolomite bedrocks, for instance, which are rich in fissures allow for rapid water travel times. These conditions are unfavourable for the removal of water contaminants. Further, the quality of water (e.g. salinity) and the soil at the geologic site (e.g. amount and solubility of arsenic content) are factors to be assessed prior to water abstraction for potable use. The TECHNEAU investigations at a test site in Delhi (India) found high levels of ammonia in surface- and groundwater. This constitutes a problem to drinking water production by BF and additional treatment will be necessary (Pekdeger *et al.*, 2008). Pollutants in soil may be of geogenic (e.g. arsenic) or anthropogenic origin (e.g. heavy metals from an industrial site, nitrate from agriculture) and render bank filtrate objectionable.

Calculating the sustainable amount and water yield from bank filtrates

In order to ensure that enough surface water is available, one should calculate the annual maximum sustainable amount (MSA in m^3/a) that can be extracted from surface water. The MSA depends on factors such as river discharge, ecological vulnerability of the surface water body, as well as the number and size of dependent cities or villages relying on the surface water downstream the BF plant. Once the MSA has been identified, the next step

involves the calculation of how much water can sustainably be produced by river bank filtration:

$$Q_{BF} = MSA/S_{BF}$$

In the equation above, S_{BF} is the BF share, i.e. the share of surface water contained in the overall produced bank filtrate Q_{BF} which largely depends on the transmissivity of the colmation layer of a riverbed. Theoretically, S_{BF} can be between 0 and 100%, but it is usually in a range of 50 and 90%. The amount of infiltrating surface water is also subject to seasonal variations and aquifers have different capacities of water storage.

Although strong seasonal variations in precipitation and run-off regimes is a phenomenon not limited to developing and newly-industrialised countries, extreme weather patterns are frequent in such countries. Climate change is believed to promote extreme weather events further. The population in developing and newly-industrialised countries is usually more vulnerable to water shortages or floodings than their counterparts in developed countries and require simple and cost-efficient solutions. BF can offer freshwater storage capacity in times of heavy precipitation (e.g. during monsoon) or elevated stream run-off (e.g. snowmelt from higher altitudes). In the subsurface, freshwater stocks are protected from evaporation and deterioration. They can be stored until dry weather conditions require groundwater abstraction to meet water demand.

It should be ensured that the BF induced ambient groundwater abstraction, i.e. $Q_{GW} = Q_{BF} \times (1-S_{BF})$ does not lead to an overuse of the aquifer. Thus, for a first assessment, a high BF share (~90%) is assumed. The calculation of S_{BF} and well yields (and thus, the number of wells needed to achieve Q_{BF}) requires information on the local hydrogeology, hydraulic conductivities of riverbed and banks, as well as information on the ambient groundwater flow field. A first assessment can be carried out using the NASRI (Natural Systems for Recharge and Infiltration) BF simulator, an evaluation tool that allows estimating the BF share based on known parameters such as hydraulic conductivity (Holzbecher *et al.*, 2008).

Overall, the design of BF systems usually requires detailed hydrogeological site investigation and knowledge about the hydrological characteristics of the catchment. Suitable sites for BF are sand and gravel aquifers with hydraulic conductivities $k_f > 10^{-4}$ m/s, a minimal thickness of 5 m and a good hydraulic connection to the adjacent surface water (TZW, 2006a). The latter is affected by dredging of the riverbed, as well as clogging and unclogging of river bed and banks. Clogging and restoration processes result from sedimentation of suspended particles and subsequent remobilisation, depending on the flow velocity of the river at the water-sediment interface. Particle load and discharge dynamics of the river might have a considerable impact on the infiltration capacity, and thus BF share. Ideally, analyses of the acquired hydrological/hydrogeological data as well as of water resources management scenarios should be supported by (sub-)catchment scale hydraulic modelling.

2.2 Elimination potential

- Developing and newly-industrialised countries are considerably affected by water quality deterioration, the elimination potential of BF can help to produce drinking water quality
- Processes by which substances are removed during subsurface passage are straining, adsorption, ion exchange, precipitation and decay

BF is considered an effective tool to remove many different substances from surface water (Partinoudi & Collins, 2007). Up to now, a deterioration of the cleaning capacity of a BF system with respect to pathogens, adsorbable or degradable substances has not been observed (TZW, 2006a). The interaction of the physical, hydrogeochemical and microbiological processes involved is complex and water quality changes during BF can be difficult to predict. In BF systems, the fate of water constituents is determined by the principles of straining/filtration, adsorption, ion exchange, precipitation/dissolution and degradation/inactivation (Mattheß, 1990; Balke & Zhu, 2008).

Straining denotes the mechanical filtration process whereby suspended matter is retained in soil based on pore throat size (larger particles are better retained than smaller particles) (Schijven *et al.*, 2002). Straining for a given particle is considered significant when the ratio of particle diameter to the median grain diameter (d_p/d_c) is greater 0.05, although straining has also been reported when the ratio was as low as 0.002 (Tufenkji, 2007). It has been observed in soil column experiments that angular media (crushed limestone) retained single particles better than rounded media (river stone), i.e. a wider range of particle sizes is removed (Barton & Buchberger, 2007). Generally speaking, the flow velocities rise and the retention efficiencies decrease with increasing soil texture permeability. Fine soils decrease flow velocity and increase contact time for adsorption, but they are also more prone to blocking. Porous texture allows for flow and offers additional binding sites. Such geologic site features (e.g. soil and rock type, heterogeneity, pore size, fissures) affect the transport of particles in the subsurface.

Adsorption, by definition, is the reversible process occurring when a gas, liquid or solid accumulates on the surface of an adsorbent or substrata. This is the case, for instance, when hydrophobic water constituents bind to the soil matrix. Sorption is a reversible process but the retardation of particles in the subsurface renders them available to biodegradation by microorganisms. Hydrogeological aquifer characteristics (e.g. hydraulic conductivity, soil texture, pore size, presence of metal hydroxides, moisture and organic content) and water quality parameters (pH, temperature) influence adsorption processes.

Ion exchange describes the exchange of dissolved ions, ions bound to a surface or sediment and the surface itself (= ion exchanger). This process is reversible

and depends on pH, temperature, surface charge and electrolyte concentration.

Precipitation occurs when insoluble compounds form and precipitate from the solution. In the subsurface, precipitation and its reverse reaction, dissolution, are often triggered by microbial respiratory activities that affect pH and redox conditions.

Complete *Biodegradation* is a form of decay carried out by microorganisms and together with *radioactive decay*, it is the only sustainable removal process. Biodegradation is the main driver for redox processes occurring during subsurface passage and is responsible for the break-down of dissolved and/or sediment-bound organic matter. The decomposition of matter leads to a successive consumption of the terminal electron acceptors (TEA), namely in the order dissolved oxygen, nitrate, manganese- and iron(hydroxy-)oxides, sulphate and dissolved inorganic carbon. Along the flow path, from the infiltration zone to the production wells, the TEA consumption can lead to the formation of distinct redox zones characterised by aerobic, denitrifying (suboxic to anoxic), manganese-, iron and sulphate reducing conditions (anoxic) and finally, methanogenesis (anaerobic) (McMahon & Chapelle, 2008). However, redox zones are not always distinct but mixed. The occurrence, location and spatial extension of the redox zones in the aquifer and their temporal dynamics strongly depend on the availability of the TEA's, temperature, concentrations of biodegradable organic carbon and retention time within the aquifer. Due to production and consumption of protons and redox components, redox reactions can trigger other reactions such as proton buffering, the already mentioned mineral precipitation/dissolution or surface complexation. Hence, they have a profound impact on the major ion composition, but also on the fate of other water constituents such as heavy metals or organic micropollutants. Incomplete biodegradation leads to the occurrence of transformation products, which in turn may also be of concern for drinking water production.

The transport behaviour of many undesired substances (e.g. heavy metals, algal toxins, pesticides, pharmaceuticals, and organics) depends on the local hydrogeochemical environment within the aquifer. For instance, the fate of heavy metals is mainly determined by surface complexation reactions, co-precipitation, redox conditions and mineral dissolution. Trace organic compounds are affected by sorption and microbial degradation. Biodegradation rates are quite different between field sites depending on water temperature and local redox conditions within the aquifer. Substances can be degradable or persistent. In some cases, concentrations may even increase. A common example for the latter is the often observed increase of dissolved iron and manganese during subsurface flow towards abstraction wells. During the biodegradation of organic matter under oxic conditions, an increase of carbon dioxide and thus, a decrease in pH may be observed. Furthermore, in pyritic aquifers, infiltration of oxygen-rich surface water can lead to an increase of sulphate. An augmentation of arsenic has sometimes

been observed in recovered water from MAR systems due to either the oxidation of As-bearing pyrite or the reductive dissolution of arsenic associated with iron(hydro-) oxide minerals.

Comprehensive and consistent databases describing in detail the fate of water constituents in BF or other MAR systems are scarce and usually focus on certain subclasses of compounds. The NASRI project (Natural and Artificial Systems for Recharge and Infiltration) that was conducted between 2002 and 2005 in the area of Berlin aimed at the development of “a comprehensive process understanding to ensure the long term sustainability of bank filtration and artificial recharge keeping in mind future requirements and threats”. NASRI results, work conducted in India and other literature has been considered in this report.

2.2.1 Temperature & pH

- Higher temperatures are deemed prevalent in most developing and newly-industrialised countries. They enhance biodegradation and promote oxygen depletion. Many removal processes are redox-dependent
- pH is a result of the interaction between the water phase and the sediment bedrock, thus, bank filtrate may potentially become more alkaline (e.g. calciferous aquifer) or more acidic (e.g. pyretic aquifers). Some removal processes are pH-dependent (e.g. calcite dissolution)

Temperature and pH are two physical water parameters that have a profound impact on water chemistry, biology and the processes that lead to the removal of contaminants in the subsurface (Wu & Nofziger, 1999; Langan *et al.*, 2001; Kirschbaum, 2006). Surface water temperature is influenced by air temperature, solar radiation, evaporation and melting ice originating from surrounding altitudes (Langan *et al.*, 2001). Also anthropogenic discharges such as cooling water from power plants can considerably impact surface water temperature. Aside from anthropogenic impacts, water temperature in rivers is influenced by the atmosphere and exfiltrating groundwater, while lakes are usually affected by the atmosphere only. A 30-year period study of a river catchment in Scotland reported a strong correlation of water and air temperature ($r^2=0.96$) and seasonal variations to lie between 0.5 and 13.5 °C (Langan *et al.*, 2001). Temperature is the driving factor for the seasonal lake stratification and thus, mass transport. Annual temperature variations in an artificial recharge pond in Germany varied between 0 and 24 °C (Massmann *et al.*, 2006). In warmer climate zones where the majority of developing and newly-industrialised countries is located, average water temperatures are higher and less subject to seasonal variations. The tropical, deep Lake Malawi in East Africa, for instance, exhibits permanent density stratification, temperatures between 24 °C in winter and 28 °C in summer and is anoxic below 220 m depth (Vollmer *et al.*, 2005).

When surface water infiltrates a groundwater system during bank filtration, the bank filtrate follows the average temperature of surface water. However, a retardation factor of about 2 in the subsurface passage needs to be considered, i.e. temperature travel times take twice as long as water travel times. Bank filtrate temperature will adopt the annual mean temperature of surface water and air, if residence times in the subsurface are sufficient (~several months). In Germany, the mean groundwater temperature is about 10 °C. Temperature extremes become effectively mitigated by bank filtration over time (Kühn & Mueller, 2000).

Water temperature has been recognised in the 1960's as a possible tracer for river water/groundwater flow patterns (Anderson, 2005). Its use has been expanded to a range of applications in hydrogeological settings such as investigations of the stream and groundwater interchange (Constantz & Stonestrom, 2003; Anderson, 2005). Groundwater temperature is influenced

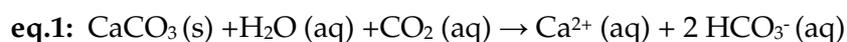
by river dynamics and changes in hydraulic conductivity, e.g. when quickly infiltrating surface water mixes with groundwater.

Groundwater temperature affects solubility, redox zone formation (e.g. cold water dissolves more oxygen), viscosity and microbial activities. Generally, microorganisms rely on adequate temperatures for proliferation (Höll, 2002; Brock, 2000). Unfavourable conditions may cause low or the ceasing of metabolic activities. While some authors reported the positive effect of higher temperatures on degradation (Grünheid *et al.*, 2008; Yuan *et al.*, 2004; Schönheinz *et al.*, 2005). Greskowiak *et al.* (2006) observed that phenazone degradation below an artificial recharge pond was better during winter than during summer months. The underlying reason was the availability of sufficient oxygen for aerobic degradation in winter months whilst the aquifer fell anoxic as soon as temperatures exceeded 14 °C. In temperature-controlled soil columns, bulk organics were shown to be degraded quickly and rather temperature-independent within the first few centimetres. However, higher temperatures appeared to promote the mineralisation of bulk and trace organics along the further infiltration path (Grünheid *et al.*, 2008).

The **pH** is defined as the negative decadic logarithm of the hydroxonium ion (H₃O⁺) concentration/activity and ranges in aqueous solutions from pH 0 (acidic) to pH 14 (alkaline). The pH is temperature-dependent and neutral at its equilibrium (pH 7, 22 °C). Since health hazards have not been described, German drinking water regulations and the WHO recommend a tolerable range between 6.5 and 9.5 with regard to technical operation (TrinkwV, 2001; WHO, 2006).

The dissolution of salts can acidify water or render it more alkaline. Surface and groundwater systems usually exhibit buffer capacities protecting them from large pH shifts. However, the buffer capacities can be exceeded as was seen in an example where a Norwegian lake used for drinking water supply naturally acidified. The weathering of sulphidic-containing gneiss bedrock formed sulphuric acid and the lake water was increasingly objectionable for potable use (Hindar & Lyderson, 1994).

Rock dissolution of calcite renders water more alkaline, a process often described by the carbonate-carbonic acid equilibrium (Appelo & Postma, 1993). Gaseous carbon dioxide (CO₂) dissolves in water until equilibrium with the air boundary is achieved. A minor fraction of the dissolved or “free” carbon dioxide reacts with water to carbonic acid (H₂CO₃). The carbonic acid dissociates into hydroxonium ions, bicarbonates (HCO₃⁻) and carbonates (CO₃²⁻). This acidification triggers calcite (CaCO₃) dissolution. At pH conditions <10, calcite increasingly dissociates into calcium and bicarbonate ions (eq. 1). When the free carbon dioxide is in balance with carbonic acid and carbonate, the carbonate-carbonic acid equilibrium is achieved.



This simplified description of the carbonate-carbonic acid equilibrium is more of technical relevance to water distribution networks and can only be an approximation to groundwater processes as it neglects the dolomite-carbonic acid equilibrium and ion-exchange reactions in the subsurface (Rathsack, 2002). If not influenced by man (e.g. by leaching of industrial landfills), the pH in aquifers is a result of the interaction between the water phase and the surrounding sediment bedrock. Bank filtrate may be rendered more alkaline in calciferous aquifers and more acidic in pyritic aquifers, when, for instance, iron sulphides become remobilised. Acidification may further destabilise the system and mobilise other heavy metals into solution. Before BF is implemented, it is recommended to study the geogenic properties of a site to evaluate a potential effect of the soil composition on the pH in bank filtrate. Further, influence by anthropogenic activities should be taken into consideration.

Many developing and newly-industrialised countries are located in zones of warmer climate. The air temperature largely affects surface water and shallow groundwater temperature. This has implications on the microflora present and the formation of redox zones, both are major factors determining degradation during bank filtration. Higher temperatures, for instance, appear to promote anoxic conditions which slow down the degradation of organic carbon and many trace elements. Further, temperature affects climate and the hydrological cycle. Run-off, the amount of precipitation and extreme weather events may severely limit agricultural activities and human prosperity. Weather extremes as seen in monsoon-affected countries require management strategies to minimise the damage by flooding/droughts, harvest stormwater and develop storage schemes (e.g. artificial aquifer recharge). Freshwater resources are often scarce in developing and newly-industrialised countries and more at risk for overuse, contamination and salinisation.

2.2.2 Suspended solids

- TSS are deemed important to developing and newly-industrialised countries given that equatorial riverine systems carry 60% of the global TSS load
- BF have a high capacity to remove suspended solids (<1 NTU)
- Low flow velocities and gravel river beds enhance the risk of colmation by TSS and thus, decreased filter performance

Suspended solids designate small particles (>0.45 µm) that - when mixed with aqueous solutions – remain in suspension (Thibodeaux *et al.*, 1993). The water quality parameter “total suspended solids” (TSS) comprises particulate organic matter (POM) and particulate inorganic matter (PIM). In water systems, suspended solids can be carriers for pollutants (e.g. heavy metals) and pathogens, hence shielding the latter from disinfection measures such as chlorination (Zhu *et al.*, 2005; Berman *et al.*, 1988). A parameter to describe suspended solids is turbidity which is often measured as nephelometric turbidity unit (NTU) or formazine nephelometric units (FNU). The German and US American drinking water standard stipulate turbidity to be less than 1 NTU (= 1 FNU). For UV disinfection, a value of less than 0.2 FNU is recommended. The WHO recommends water turbidity to be less than 5 NTU for drinking water and less than 1 NTU for effective chlorination.

BF has a high capacity to remove suspended solids from water due to the filtration effect that occurs predominantly at the water sediment interface. This is mediated by straining of larger particles and physical processes such as Van-der-Waals forces retaining smaller particles. In general, no further treatment is necessary. Wang (2002) found that turbidity in BF wells located in a sand-gravel aquifer was less than 1 NTU even when the turbidity in the river water was up to 1000 NTU. An increase in suspended solids in surface water is usually observed during flooding and storm water events. In the River Rhine, variations in suspended solids between 10 g/m³ and 400 g/m³ (~1 and 100 FNU) were observed, nonetheless the turbidity in well water remained <0.05 FNU (Schubert, 2002).

Excessive amounts of suspended solids may lead to clogging of the water-sediment interface. In Berlin, micro-sieving or flocculation/rapid filtration pre-treatment of surface water is carried out (mainly during summer months with higher amounts of algal biomass) to prolong maintenance intervals of the artificial recharge sites. The aim is to achieve TSS values of <2 mg/L for the infiltrating water (<1 FNU). Depending on the flow velocity of a stream, shear forces at the water-sediment boundary may naturally counteract clogging.

Beusen *et al.* (2005) developed a model to describe the transport of suspended solids (and associated particulate nutrients) from rivers to coastal seas worldwide taking into consideration grass- and wetland contributions, precipitation and lithology. The river export of TSS worldwide was calculated

to be 19 Pg yr⁻¹ (1 Pg = 1 Petagram = 1 billion tons) and the three main contributors for particulate nutrient export being Asia (50%), South America (20%) and Africa (12%). This illustrates that rivers in the southern hemisphere carry large quantities of suspended matter. The finding is especially true for equatorial riverine systems which are estimated to carry about 60% of the world's total suspended load originating from the Indo-Pacific archipelago where high relief and rainfall result in high sediment yields (Meybeck, 1988; Ramesh *et al.* 1995). When applying BF/AR schemes in developing or newly-industrialised countries, these elevated loads in suspended solids should be taken into account and source water may require a pre-treatment step.



Fig. 1: Rivers in the southern hemisphere carry high loads of suspended solids (e.g. the Yamuna River in Delhi).

Colmation

Clogging is a process during which the interstices in a riverbed become blocked due to particle sedimentation. This effect, which is enhanced at slow flow velocities, can be both beneficial in terms of promoting biodegradation and deteriorating by reducing the hydraulic conductivity of the infiltration zone (Hiscock & Grischek, 2002) To which extent and pace this clogging process (colmation) occurs, depends on the amount and dimensions of the suspended solids, the river flow, sediment texture and hydraulic gradient. From an engineering point of view, the characteristics of interest are the permeability and thickness of the riverbed sediments but for a holistic evaluation, biological activity and chemical processes should be likewise taken into consideration (Velickovic, 2005).

The run-off regime which is characterised by the amount, frequency, duration and time of run-off conditions largely determines self-cleaning potential (Schubert, 2006). Periods of elevated water levels in streams may promote

self-purification by so-called streambed scouring as the result of shear forces. Stuyfzand *et al.* (2006) reported that in the Netherlands, sandy river beds can sustain a higher recharge rate for a longer time than gravels beds, likely because deposits remain on the surface of the sediment and are better sheared off by river flow.

Other natural self-purification processes comprise the exfiltration of groundwater into the river and (micro-)biological grazing activities. However, during BF the operation of wells causes locally a permanent drawdown in groundwater levels and creates unidirectional flow towards the aquifer, thereby enhancing colmation. For countries with high loads in TSS, this can mean a decrease in yield and filter performance. Since mechanical cleaning measures are not enduring, clogging of riverbeds is best proactively addressed by a reduction in pumping rate and water quality improvements (Schubert, 2006).

2.2.3 Pathogens

- Pathogens are the most pressing issue to developing and newly-industrialised countries
- The processes affecting pathogen fate during subsurface passage are straining, sorption and inactivation
- For pathogen removal, travel times should be at least 50 d to 100 d and fine soil texture exhibiting filter properties is favourable. Longer travel distances may be required in rather coarse (gravel) aquifers

Pathogens comprise microorganisms such as bacteria, viruses and protozoa but also larger parasites like helminths causing illness in humans and animals. An estimated 2.2 million people die annually as the result of poor water quality, sanitation and hygiene, of which 90% are children and virtually all deaths are in developing countries (Ashbolt, 2004, Santo Domingo & Ashbolt, 2008). In many cases, this is due to infectious diarrhoea caused by pathogens that are adapted to the intestinal tract of warm-blooded, mammalian hosts (Santo Domingo & Ashbolt, 2008).

When the cycle of oral uptake and excretion of pathogens into the waterways had been understood, a faecal indicator concept was implemented in the early 20th century to monitor microbial water quality (Stevens *et al.*, 2003). The testing for enterobacteria, i.e. bacteria commonly found in the intestinal tract, such as *Escherichia coli* and other coliforms, as well as intestinal enterococci, is nowadays used worldwide to indicate the presence of enteric pathogens.

Taking the potential infectivity into account, the German Drinking Water guidelines stipulate - in accordance with WHO recommendations for drinking water and in concordance with the EC Drinking Water directive - the absence of the indicators *E. coli*, coliforms and enterococci in 100 ml water meant for human use (TrinkwV, 2001; WHO, 2006). The pathogen concentrations in the environment are highly variable encompassing several orders of magnitude, therefore, their numbers and their removal are commonly expressed on a logarithmic scale. Due to the high variances of pathogen concentrations found and the sometimes low infective doses, a 2-log removal (99%) is often not sufficient. In surface water, the number of somatic bacteriophages (as plaque forming units) - which have been proposed as surrogate organisms to indicate pathogenic viruses - was as high as 1.2×10^5 pfu/100 ml in the Indian river Yamuna (Sprenger *et al.*, 2009) while for lake Wannsee in Berlin, a maximum of 800 pfu/100 ml has been observed (Lopez-Pila & Szewzyk, 2002). In the study by Sprenger *et al.* (2009) pathogenic viruses (Hepatitis A viruses, Hepatitis E viruses, noroviruses and adenoviruses) were also present in the Yamuna river. Noroviruses and adenoviruses were found at concentrations of 3.6×10^4 and 5.4×10^4 genome copies/100 ml respectively.

Although the indicator concept persists as a useful, cost-effective tool in water analysis, there is no indicator organism that could represent the variety of

waterborne pathogens with their different growth requirements and survival strategies. In comparison to the simple-structured viruses or some protozoan pathogens capable of adapting dormant, robust stages (e.g. *Cryptosporidium* oocysts, *Giardia* cysts), indicator bacteria are rather vulnerable to environmental stress and disinfection measures. Thus, their absence does not automatically rule out the presence of pathogens (Grabow, 1996). Viruses and protozoa can both already be infective at low doses and are capable to survive long-term in water systems. Viruses are found to be moderately and protozoa highly resistant to chlorination (WHO, 2002a). Several “faecal”, i.e. thermotolerant, coliforms have been recognised to also occur naturally in the environment, thus, only *E. coli* is still regarded as reliable indicator for a faecal pollution.



Fig. 2: Livestock can excrete pathogens and should not be kept near watersheds

The groundwater habitat accommodates a rich diversity of microorganisms (Brockman & Murray, 1997; Goldscheider *et al.*, 2006). Human pathogens are not indigenous to the groundwater environment and are, if present, likely a result of the intrusion of faecally-contaminated surface water, sewage and manure (Keswick, 1984). The oligotrophic conditions and low temperature found in groundwater systems are unfavourable for pathogens and prevent their proliferation in the subsurface. However, low temperatures promote pathogen survival. Pathogens further increase their chances for survival by adopting resilient, dormant states or associating with biofilms. The latter consist of microbial communities embedded in their viscous, extracellular polymeric substances attached to surfaces. Biofilms offer advantages to organisms like facilitated nutrient access and protection from grazing protozoa (Donlan, 2002; Hall-Stoodley *et al.*, 2004; Foppen & Schijven, 2006).

When pathogen-harboring biofilm chunks slough off or when travel times from a source of contamination are too short, abstraction wells are at risk for contamination. In the past, numerous incidents of well contamination have

been reported (Schijven *et al.*, 2002; Hrudey & Hrudey, 2004). Nonetheless, subsurface passage has been suggested and demonstrated to reduce, if not eliminate, the pathogen load from surface waters. Pathogen fate and transport in the groundwater environment is foremost governed by interactions with the solid phase (e.g. straining, filtration, sorption) and inactivation (i.e. die-off) (Tufenkji, 2007).

Straining depends on the ratio of the diameter of media and the diameter of pathogenic particles (protozoa>bacteria>viruses). It has been suggested to be mostly significant for protozoa, less important for bacteria, negligible for bacterial spores and insignificant for viruses where no clogging occurs (Berger, 2002). Since helminths are not a concern in industrialised countries that contribute the bulk of published literature, studies on their removal during bank filtration are scarce. However, given that helminth eggs are much larger (25-150 µm) than protozoan oocysts (*Cryptosporidium parvum* oocysts: 4-6 µm), they are also likely subject to straining processes.

Several mathematic models have been used to predict the fate of pathogens in the subsurface but are all limited in one way or the other. For instance, the colloid filtration theory is limited to conditions favourable for deposition only and does not consider straining or detachment (Tufenkji, 2007). Factors to be taken into account include physical forces (Van-der-Waals forces, convective transport, dispersion, diffusion) (Ginn *et al.*, 2002; Foppen *et al.*, 2007), hydraulics (flow velocity and direction), physico-chemical filtration and sediment texture, heterogeneity, association with suspended matter (Mahler *et al.*, 2000), inactivation kinetics and grazing activities, mechanisms of microbial attachment and detachment (Tufenkji, 2007; Matthess *et al.*, 1988).

Microbial adhesion and the function of the complex cell surface structures are not yet fully understood to predict pathogen fate in porous media (Tufenkji, 2007). The more important mode of attachment is the reversible adsorption to sediments, a mechanism, whereby particles become retarded in the subsurface. Factors promoting adsorption are high ionic strength, low flow velocities, low pH values (reduced electric repulsion) and the presence of multivalent cations or metals enabling salt bridge formation or sorption to ferric hydroxides (Fontes *et al.*, 1991). Soluble organics such as proteins may prepare surfaces for colonisation or offer protection, but the generally negatively-charged organic matter counteracts adsorption by competing with negatively-charged pathogens for attachment sites (Schijven *et al.*, 2002; Pieper *et al.*, 1997; Sobsey, 1983). Low pH values promote adsorption (e.g. for viruses) whereas alkaline conditions hinder adsorption or trigger detachment (Matthess *et al.*, 1988). Adsorption is further strongly influenced by species characteristics such as size, isoelectric point, surface composition/charge and the occurrence in resilient states (spores, cysts, oocysts) (McLeod *et al.*, 2004; Tufenkji, 2007).

Once retained by sorption, straining or other filtration processes, pathogens may become inactivated by starvation, by microbially-excreted proteolytic enzymes or become assimilated by grazers (Gerba & Bitton, 1984; Gounot,

1994). It has been suggested that survival is affected by pH, moisture and organic content while retention is affected by ionic strength, pore size and clay content (Sobsey, 1983, Gerba & Bitton, 1984).

There are numerous studies on pathogens and indicator removal during subsurface travel (Weiss *et al.*, 2005, Schijven *et al.*, 2002, Medema *et al.*, 2000). An overview on the removal potential of BF is provided in this study (Appendix). However, the list is not exhaustive and due to more or less detailed site descriptions provided, a direct comparison is often difficult. Travel distance (metres = m) and travel time (days = d) are the two parameters easy to measure and frequently used to describe removal efficiency during subsurface travel. Elimination, inactivation and removal are not always properly defined in literature and are given in percentage, log-removal and elimination/inactivation rates. Log-removals denote herein the reduction of pathogen concentrations from surface water to the concentration in bank filtrate after subsurface passage.

For both, viruses and bacteria, the WHO (2002a) considered BF capable to achieve a 3-log and 4-log removal after 2 m and 4 m respectively. The WHO even deemed a 4-log reduction for protozoa possible whilst the USEPA (2003) credited bank filtration only for 0.5 and 1-log reduction after 7.6 m and 15.2 m respectively for protozoa using an unconfined sand aquifer with at least 10% fines. Although the mentioned travel paths appear rather short, the infiltration zone is recognised to exhibit a superior cleaning capacity (Schijven *et al.*, 1999; Sprenger *et al.*, 2009). The literature reviewed and compiled in table 10 (Appendix) illustrates the broad removal range of 0.5 to 8-log₁₀ for viruses, 3 to 6 log₁₀ for non-sporeforming bacteria, 0.4 to >4.9-log₁₀ removal for spore-forming bacteria and an estimated 0.5 to 4- log₁₀ for protozoa. The compilation suggested that non-sporeformers are better removed than sporeformers and protozoan *Giardia* cysts better (2-log₁₀) than *Cryptosporidium* oocysts (0.5 to 1.5 log₁₀), possibly because they are twice as large.

Bank filtration is in principle an efficient method for pathogen removal as long as flow path and time are sufficient, however, occasional failure may occur and additional treatment such as disinfection may be necessary (Schijven *et al.*, 2002). While BF is often regarded as pre-treatment (e.g. in the United States), in Berlin (Germany) - where BF has been practised for 100 years – bank filtrate receives no disinfection and outbreaks have not been observed.

For BF design, system parameters that are to be considered for efficient pathogen removal are long infiltration paths, low heterogeneity, fine to middle grained sediment, presence of complexing iron and aluminium hydro(oxides) and low flow velocities (Schijven *et al.*, 2002; Schmidt *et al.*, 2003). Matthess *et al.* (1988) suggested that a 3-log removal corresponds to a residence time of 50 days in sand and gravel aquifers. In Germany, groundwater wells are located within groundwater protection zones (I-III) and the dimensions of zone II are defined such that water has a residence time of at least 50 days. This concept is based on the experience that the 50-

days interval is sufficient to ensure the elimination of pathogens (Matthess *et al.*, 1988). For bank filtration, minimum travel and retention times between 50-100 days have been suggested to be efficient for pathogen removal (Grischek *et al.*, 2002; Schijven *et al.*, 2002; Matthess *et al.*, 1988; Schlosser, 1991).

In many developing and even newly-industrialised countries, surface waters are used concomitantly as drinking water source and for discharging sewage, the drinking water treatment processes being insufficient or rudimentary. As a result of lacking sanitation and access to safe water, the main burden of disease and death is in the developing world. At times of extreme temperature and rainfall events (e.g. monsoon, droughts), water quality can further deteriorate. Surface waters are depleted during dry seasons often failing to compensate anthropogenic pollution. During wet seasons, stormwater carries high loads of organics, sediments and also remobilised pathogens. Warm climate and eutrophic water bodies promote proliferation of certain pathogens and in combination with poor hygiene, also give rise to species no longer seen in industrialised countries (e.g. parasitic worms). BF is considered particularly useful in developing and newly-industrialised countries to improve water quality and remove pathogens either as method of pre-treatment or even as main treatment. However, disinfection as post-treatment is highly recommended.

Bank filtration holds good potential for pathogen removal but BF schemes require thorough design in terms of long travel paths, retention time (50 to 100 days) and soil texture (sand aquifers) in order to comply with the strict guidelines that stipulate several log-removal for microbial contaminants.

2.2.4 Algal toxins

- Warm, eutrophic waters are deemed to promote harmful algal blooms and thus, algal toxins are considered highly relevant in developing and newly-industrialised countries
- For cell-bound toxins (e.g. microcystins) straining of the cells is an efficient BF process (reduction of >99% within the first meters)
- Biodegradation of extracellular microcystin is usually rapid (half lives up to a few days), adverse conditions are anaerobic conditions, low temperatures (<10°C) and no previous exposure

Algal toxins are a heterogenic group of toxic metabolites produced by some 50 different species comprising algae and cyanobacteria (“blue-green algae”). In freshwater, cyanobacteria are of most concern producing several toxins such as microcystins, anatoxins and nodularins. Cyanotoxins are categorised by their mode of action. The major types are liver-damaging hepatotoxins (e.g. microcystin, anatoxin), cell-damaging cytotoxins (e.g. cylindrospermopsin) and neurotoxins (e.g. nodularin) impairing the nervous system. Literature on algal toxins has mainly focused on the highly toxic microcystin-LR (LD₅₀ *i.p.* mouse value of 50 µg/kg) for which the WHO recommends a guideline value of 1 µg/l in drinking water (WHO, 2006). In 1996, 101 patients in a Brazilian treatment centre became ill and about 50 died after coming in contact with dialysis water that was contaminated with the blue-green algae *Microcystis aeruginosa* (Azevedo *et al.*, 2002; Jochimsen *et al.* 1998). This incident spurred the amendment of the Brazilian drinking water regulation (Ministério da Saúde do Brasil, 2004) by implementing not only a threshold for microcystin-LR but additional threshold values for saxitoxin (3 µg/l) and cylindrospermopsin (15 µg/l).

Algal blooms are per se not an unusual phenomenon but there has been an increased number of reports on health-impairing, so-called “harmful algal blooms” (HAB) in recent years. This may partly be due to improved analytical methods and public awareness, however, global warming (Paerl & Huisman, 2008; Paul, 2008) and the pollution of waterways (Charlton *et al.*, 2002) have been suggested to be factors promoting algal blooms. Standing water bodies such as lakes are more vulnerable than streams. Ganf & Rea (2007) investigated algal bloom potential in tropical rivers with low nutrient levels and found that the longer the rivers, the slower the flow, the greater the availability of nutrients and the higher the potential for algal blooms. In a nation-wide investigation of German surface waters between 1995 and 1997, microcystins were detected in 52% of 120 investigated lakes and dams, whilst the neurotoxins anatoxin-a and PSP toxin were present up to 26% and 34% respectively (Hiller & Luckas, 2005).

Algal growth is usually limited by the availability of phosphorus and the prevalence of species depends on temperature and seasons (Hoehn & Long). For the Australian Murray-Darling Basin, nitrogen has been identified to limit algal growth as often as phosphorus and stream flow manipulation has been

suggested to counteract long residence times and stratification (Davis & Koop, 2001). Surface water concentrations of cyanobacterial toxins show great variations and general predictions are difficult. During seasons without cyanobacterial or algal blooms, critical concentrations are usually not exceeded. Whilst for microcystins (MCYST), a maximum surface water concentration from scum-forming species of more than 10 mg/L has been observed Chorus & Fastner (2001), during the NASRI studies conducted at Lake Wannsee in Berlin between 2002 and 2005, concentrations were rarely found to exceed 10 µg/l even in summer months. In another example from Japan, lake water supplying 14 million people was shown from 1998 to 2000 to exhibit a gradual increase in cell density of *Microcystis spp.* Generally, concentrations of microcystin remained below 5 µg/l with an observed maximum concentration in a 3-year-observation period of 36 µg/l (Ozawa *et al.*, 2005).

Water utilities measure biovolumes to deduct toxin concentrations in source water (House *et al.*, 2004; Van Baalen & du Preez, 2005). For Berlin, a cyanobacterial biovolume of 5 mm³/l has been proposed as value of action taking by the NASRI project to indicate the need to further investigate actual toxin concentrations and the distribution of cyanobacteria within the surface water body (Chorus & Bartel, 2006).

In healthy cyanobacterial populations, more than 90% of microcystin is present **intracellular** (Sivonen & Jones, 1999). However, cell walls may become disrupted (e.g. by algicides), whereby toxins are released. Some cyanotoxins such as cylindrospermopsin can generally occur **extracellular**.

Bank filtration can be an efficient alternative to conventional water treatment to reduce cyanotoxins. The main process for the reduction of intracellular cyanotoxins is straining. Removal by more than 99.9% within the first 10 cm of middle to coarse grained sands has been demonstrated for intracellular microcystin (Grützmacher *et al.*, 2007). In a study using surficial esker sediment filter columns, 97.8% of microcystis cells were retained after 30 cm sediment passage at a flow velocity of 0.9 m/d (Lahti *et al.*, 1998). This is in line with observations by Bricelj & Sedmak (2001) who reported 92.8 to 97.3% removal after 1 m passage in gravel-packed columns at 2 m/d.

In fact, biodegradation is the only sustainable process for toxin elimination which is promoted by retardation. Adsorption has been observed to be best in clay/silt and soil rich in organic content (Miller *et al.*, 2005; Lahti *et al.*, 1998; Grützmacher *et al.*, 2007). For MCYST adsorption, kd-values were shown to range from 0.076 ml/g (pure quartz sand) to 11.6 ml/g (aquifer material from Lake Wannsee, Berlin) (Grützmacher *et al.*, 2007). Temperature and redox conditions also influence toxin degradation rates. In lab-scale experiments, half-lives of less than 1 day under aerobic conditions have been observed whilst during anaerobic conditions half-lives could be more than 25 days. Under optimal conditions, high concentrations of microcystin (>100 µg/l) are considered to be efficiently reduced by bank filtration below the WHO guideline value within 10 days. However, at less favourable conditions,

residence times of up to 3 months are deemed necessary (Grützmacher *et al.*, 2007). Lahti *et al.* (1998) reported that 30-60 µg microcystins/l were eliminated by 98-99.9% within 9-14 days in surficial esker sediment columns whilst removal in the coarser subsoil was less efficient (30-90%). Complete removal of nodularin and microcystin-LR has been reported within 10-16 days in soil of high organic content whilst retention was inefficient in sandy soil (98.5% sand) columns (Miller & Fallowfield, 2001).

Studies on algal toxins other than microcystin are scarce. However, recently extracellular cylindrospermopsin (feed concentration: 10 µg/l) has been demonstrated to be efficiently removed in aerobic pond sand (92%) and aquifer sediment filled columns (98%) after 40 days of circulation (Klitzke *et al.*, *in prep*). However, degradation preceded a lag-phase of 20 days. Cylindrospermopsin is cyanotoxin occurring extracellular and has been detected in concentration of 12 µg/l in surface water (Rücker *et al.*, 2007).

Degradation efficiency may also vary from site to site. The availability of co-nutrients and necessary lag-times of nutrient adaptation have been suggested to explain degradation differences in different soils (Dillon *et al.*, 2002, Jones *et al.*, 1994). At two bank filtration sites in Finland characterised by coarse soil sediment, microcystin was still found in 100 m distance to banks (Lathi *et al.*, 1998). Grützmacher *et al.* (2007) considered bank filtration effective to meet the WHO guideline value of 1 µg/l for microcystin if initial concentrations do not exceed 500 µg/l, retention times are >9 days and the (aerobic) groundwater system consists of fine to medium sand with prevailing temperature higher than 15 °C.

The vast amount of literature that had been published on algal toxins has focused on cyanotoxins and was conducted in industrialised countries. Although studies on the fate of other algal toxins during subsurface passage are scarce, the few studies indicate that degradation efficiency and sorption may be similar. Studies from Asia, Africa and South America began only to appear in the 1990's (Sivonen & Jones, 1999) confirming that harmful algal blooms are a problem worldwide. Since promoting factors such as eutrophic water bodies and warm temperatures are prevalent in many developing and newly-industrialised countries; the problem may be even more severe. Thus, bank filtration could be a useful tool to purify source water from intracellular and extracellular toxins in these countries.

2.2.5 Nutrients (C, N, P)

The elements carbon, nitrogen and phosphorus are primary nutrients for organisms and plants. At the concentrations found in surface and groundwater, they are not harmful (the exceptions being nitrate and nitrite). In excess, they may impair water taste, odour and colour. Their presence in water needs to be primarily controlled as they determine microbial growth. Another reason for nutrient control in water is the precursor function of carbonic compounds for harmful disinfection by-products which can be formed during advanced drinking water treatment. The availability of all three major nutrients to microorganisms affects the extent of metabolic activity (and thus, ecosystem stability) and contaminant degradation during bank filtration.

2.2.5.1 Carbon

- In many developing and newly-industrialised countries, the lack of wastewater treatment and sanitation results in high organic pollution of rivers
- DOC removal between 24 and 50% has been reported for bank filtration with the most efficient removal in the oxic infiltration zone.
- Organic load from infiltrate will be biodegraded under oxygen depletion resulting in anoxic conditions. This process is accelerated by higher temperatures and believed to be common in developing and newly-industrialised countries.

Carbon is present in all organic compounds and known organisms. Autotrophic organisms (e.g. plants, algae) can derive carbon from inorganic sources (e.g. carbon dioxide); all others (including humans) are heterotrophs relying on organic carbon uptake for their nutrition. Total carbon (TC) consists of total organic carbon (TOC) and total inorganic carbon (TIC). Although carbon is a constituent of organic water pollutants (Ch. 2.2.8 Organic micropollutants) and a precursor of disinfection by-products, the emphasis is placed on the significance of organic carbon as a nutrient. Guideline values have not been suggested by the WHO. The German drinking water regulations recommend TOC levels should not exhibit "abnormal changes". A guideline value of <1.5 mg/L TOC has been recommended for copper-coated distribution systems at risk for corrosion (i.e. $\text{pH} \leq 7.4$) (TrinkwV, 2001). Further, a guideline value of <2.5 mg/L for DOC is recommended in the technical rule W 290 for source water prior to chlorination by the German Technical and Scientific Association for Gas and Water (DVGW, 2005) to avoid the formation of disinfection by-products. Similarly, in the US EPA Disinfectants and Disinfection By-Products Rule, it is recommended that source water should not exceed 2 mg TOC/l prior to chlorination (USEPA, 2001).

Total inorganic carbon comprise the species CO_2 , H_2CO_3 , HCO_3^- and CO_3^{2-} which play an important role for the carbonate-carbonic acid equilibrium and water pH as discussed earlier (Ch. 2.2.1 Temperature & pH). The decline in groundwater pH may indicate the release of CO_2 due to aerobic biodegradation in the subsurface (Jekel, 2006). For instance, under anaerobic conditions, organic matter can be degraded by methane bacteria converting CO_2 into gaseous methane (CH_4). The latter may serve as the sole source for carbon and energy to methanotrophic bacteria. The metabolisation of TIC is of minor importance to bank filtration.

High concentrations of organic carbon in water are to be avoided for microbial stability, to prevent shifts in redox and pH conditions, ion remobilisation from sediments and water treatment (DBP formation, membrane blocking/fouling etc.) The practice of disinfection (e.g. chlorination, UV irradiation, ozonation) provides hygienically safe water but does concomitantly change the water chemistry. The oxidants chlorine and ozone can react with organic matter to harmful substances; so-called disinfection by-products (Chapter 2.2.8.6 Disinfection by-products). Furthermore, the oxidation of organic compounds by ozonation and UV treatment may break down complex structures, thus, they can increase the bioavailability of carbon and promote microbial regrowth after final treatment. The following table 1 provides an overview of the different parameters used to describe the nature of carbon compounds in water.

Table 1: Common parameters for carbon in water analytics

Parameter	Description
Total Carbon (TC)	All organic and inorganic carbon (TOC + TIC)
Total Inorganic Carbon (TIC)	Sum of inorganic carbon species in a solution (CO_2 , H_2CO_3 , HCO_3^- , CO_3^{2-})
Total Organic Carbon (TOC)	Sum of carbon bound in organic compounds (TC-TIC=TOC)
Dissolved Organic Carbon (DOC)	Organic carbon that can pass 0.45 μm (<i>rarely</i> : 0.22 μm) pore filters
Biodegradable Dissolved Organic Carbon (BDOC)	Biodegradable fraction of DOC
Natural Organic Matter (NOM)	Humic substances, sedimentary and dissolved organic matter
Spectral Absorption Coefficient at 254 nm (SAK_{254} as m^{-1})	Alternative for TOC determination by measurement of UV absorption, also used to characterise humic substances
Spectral Absorption Coefficient at 436 nm (SAK_{436} as m^{-1})	Parameter for colour, used to characterise humic substances

TOC is a sum parameter denoting all organic carbon including dissolved + colloidal (<0.45 μm , *rarely*: <0.22 μm), particulate (>0.45 μm , *rarely*: >0.22 μm)

and volatile (purgeable) organic carbon. It often serves as indicator parameter for the organic load in aquatic systems and as surrogate for “natural organic matter” (NOM) which is difficult to measure. NOM is organic matter found in natural waters (e.g. lakes, rivers, reservoirs) and originates from decaying organisms, plant and animal material. In pristine waters, TOC ranges between 1 and 2 mg/L, between 2 and 10 mg/L in river water and TOC levels higher than 10 mg/L characterise heavily polluted water. The concentration in surface waters is influenced by seasonal variations (i.e. TOC increase in summer months) and run-off events.

One may further distinguish organic carbon into the parameters total organic carbon (TOC), dissolved organic carbon (DOC) and biodegradable dissolved organic carbon (BDOC). An alternative for TOC determination is the parameter SAK₂₅₄ measuring UV absorption. In combination with SAK₄₃₆, a parameter for colour, the absorption coefficients are used to characterise humic substances. In German drinking water guidelines, a threshold for SAK₄₃₆ of 0.5 m⁻¹ applies.

DOC describes the dissolved and colloidal fraction of organic carbon smaller than 0.45 µm (*rarely*: 0.22 µm). The most stable fraction of DOC has been reported to be constituted by humic substances (50-80%) which are humus-derived degradation products from plant and animal tissue (V.-Balogh *et al.*, 2003). Elevated concentrations of humic substances (as found in swamps) give water an objectionable taste, odour and colour. They can chelate multivalent ions such as Mg²⁺, Ca²⁺ and Fe²⁺, whereby these ions do not become precipitated but remain in solution and available to plants and other organisms. The complex-building with heavy metals (e.g. iron) hinders their removal during drinking water treatment.

In the NASRI project, Liquid Chromatography - Organic Carbon Detection (LC-OCD) was used to differentiate DOC according to molecular size. It was shown for two different bank filtration sites in Berlin (Lake Tegel and Lake Wannsee), that on average the DOC in lake water consisted of 46-48% humic substances (HS), 22% HS-building blocks (HS-BB), 18-20% neutrals/hydrophobics, 8.7-8.8% polysaccharides (PS) and 3.5-3.7% low molecular acids (LMA). Seasonal variations in composition were observed in lake water showing higher levels of HS in winter (~50%) and slightly lowered levels in neutrals/hydrophobics, HS-BB and PS. Factors affecting DOC composition and levels in the investigated surface water were precipitation, influence of tributaries and the appearance of organic carbon linked to algal blooms (Jekel, 2006). An overall increase of DOC levels in European and North American surface waters has been observed in recent years. Out of the possible drivers (e.g. temperature, hydrology, SO₄²⁻ and Cl deposition), the decrease of sulphate deposition since the mid-seventies was found linked significantly to the increase in organic matter (Erlandsson *et al.*, 2008; Monteith *et al.*, 2007).

BDOC, which has been reported to account for approx. 20-50% of DOC in surface water (Servais *et al.*, 1989), is usually readily degraded under oxic

conditions during the first metres of infiltration into an aquifer. Polysaccharide concentrations of 0.6-0.7 mg/L have been reported to be fast and efficiently removed (~100%) during bank filtration whilst there was only partial degradation of other fractions (Jekel, 2006).

Bank filtration is regarded an efficient tool for the removal of organic matter. Based on 100 years of experience in Berlin, the removal of DOC is primarily ascribed to degradation processes (Jekel, 2006). The DOC elimination during bank filtration depends on the initial concentration in surface water, aquifer transmissivity and the retention time in the subsurface (Lenk *et al.*, 2005). It is further influenced by temperature, redox zonation and the composition of DOC (degradable or non-degradable) (Lenk *et al.*, 2005, Weiss *et al.*, 2004, Jekel, 2006).

The initial concentration in surface water can vary significantly according to anthropogenic influences and the impact of vegetation and wetlands. Lenk *et al.* (2005) compared 31 bank filtration sites from Germany, Austria, Switzerland and France and observed DOC concentrations in surface water to range between 1.4 and 9 mg/L with an average of 4.39 mg/L. They observed a trend for increased DOC removal efficiency with increasing surface water concentration, however, a system's removal potential was suggested to be limited at input concentrations higher 8 mg/L.

The same authors developed a non-linear regression model formula (eq. 2) which is based on surface concentration, transmissivity and retention time and had been derived from 43 observation wells ($R^2 = 0.74$) to calculate DOC elimination during bank filtration as follows:

$$\text{eq. 2: } Y = -0.503 + 0.811 \ln(X_1) + 0.236 X_2^{0.437} + 7.428 X_4$$

Y = DOC elimination (mg/L)
X₁ = DOC concentration in surface water (mg/L)
X₂ = retention time in the subsurface (d)
X₄ = transmissivity (m²/s)

An alternative was suggested (eq. 3) for sites where travel distance is easier to determine than retention time:

$$\text{eq. 3: } Y = -0.999 + 1.568 \ln(X_1) + 0.033X_3^{0.737} + 3.807 X_4$$

Y = DOC elimination (mg/L)
X₁ = DOC concentration in surface water (mg/L)
X₃ = length of travel distance (m)
X₄ = transmissivity (m²/s)

In 60 observation wells investigated by Lenk *et al.*, (2005), the average DOC elimination was found to be 2.1 mg/L (~46%). This is in line with other studies reporting about 50% DOC removal during bank filtration (Wang, 2002; Kühn & Müller, 2000, Ziegler, 2001; Drewes & Summers, 2002). Depending on travel time and redox conditions, the DOC removal efficiency observed in the NASRI project was between 24-44% (Jekel, 2006). In Berlin, the DOC levels in lake water ranged from 5.5 to 9 mg/L (mean: 7.1 mg/L) and from 6.5 to 8.5 mg/L (mean: 7.17 mg/L) for Lake Wannsee and Lake Tegel respectively. At the BF site in Berlin, then on average higher DOC levels in source water coincided with comparably lower removal rates indicating the involvement of other factors limiting degradation. In the production well with the highest achievable removal (44%), water had undergone an unusual long oxic passage and a retention time between 2-4 months (~23-38 m infiltration path) (Jekel, 2006). Under anoxic conditions, usually a long retention time is recommended whilst a short oxic passage can already reduce the DOC by 35-40% (Lenk *et al.*, 2005). For an evaluation and comparison of DOC removal, a mixing of different fractions in the well has to be taken into consideration. For instance, near Lake Wannsee, abstracted well water (average DOC concentration: 3.55 mg/L) was constituted by only a quarter of "young" bank filtrate (4 mg/L), 34% "old" bank filtrate (4.9 mg/L) and 43% was ambient groundwater of lower concentrations.

Some studies also investigated the removal of different DOC fractions (not all under BF conditions) and reported rather high removal rates for soil passage. In the United States, 50-90% of the biodegradable fraction of NOM was shown to be removed during bank filtration at three Midwestern US drinking water utilities with no removal preference observed for hydrophobic or hydrophilic compounds (Weiss *et al.*, 2004). Alborzfar *et al.* (2001) reported that organic matter in humic groundwater that had been sprinkled onto an infiltration field was reduced by 79% from 105 mg C/l down to 20 mg/L after 0.5 m subsurface passage in the unsaturated zone and after further 2.5 m by 97.4% to a residual of 2.7 mg C/l in a shallow aquifer. Jekel (2006) reported that near Lake Tegel (Berlin), bank filtration removed 30% of humic substances although it is regarded a rather non-degradable fraction. It was shown during soil aquifer treatment (SAT), that DOC from sewage effluent was reduced by 90% after passage through a 37 m vadose zone (Wilson *et al.*, 1995).

Redox conditions largely influence biodegradation during bank filtration (Schwarzenbach *et al.*, 1983; Jekel, 2006; Lenk *et al.*, 2005). In the subsurface, dissolved and sedimentary organic matter is concomitantly degraded depending on the availability of electron acceptors and the reactivity of organic material. The upper layers (or infiltration zone) where oxic conditions prevail are particularly efficient in DOC removal. Complex compounds may require long retention times for degradation under anoxic or anaerobic conditions (Lenk *et al.*, 2005). Grünheid *et al.* (2005) recommended travel times of ≥ 2 weeks under aerobic conditions and ≥ 3 months under anaerobic conditions. Even then, an apparently non-degradable fraction of DOC remained. Regardless of redox conditions, DOC concentrations were shown

to be reduced down to a residual of 4.7 mg/L with an initial DOC concentration in surface water of approx. 7.4 mg/L (Grünheid *et al.*, 2005).

Bank filtration alters the composition of organic matter. Miettinen *et al.* (1994) observed effective reduction in colour-giving and UV absorbing substances and even reported that bank filtration of humus-rich lake water rather changed the quality or composition of organic matter than its total amount. A shift from higher to lower molecular weights has also been reported by Ziegler & Jekel (2001).

Assuming that in developing and newly-industrialised countries surface water is often intensively used but not balanced by water treatment and management, surface waters must be expected to be heavily polluted with organic carbon compounds such as excrements, decaying plants and animals. When surface water rich in carbon infiltrates into an aquifer, biodegradation processes may quickly deplete oxygen and turn redox conditions anoxic/anaerobic, thus affecting degradation efficiency. The break-down of organic matter is furthermore catalysed by higher temperatures. There is up to now no evidence for a deterioration over time in cleaning capacity of BF systems with respect to degradable substances (TZW, 2006a). Experience in Europe, however, but the experience in Europe has shown that under anaerobic conditions, long travel times of at least 3 months may be necessary for a complete degradation of BDOC (Grünheid *et al.*, 2005) and that a non-degradable residual remains. The composition of TOC found in surface waters (degradable and non-degradable components) needs to be investigated as this may differ from region to region.

2.2.5.2 Nitrogen

- Fertiliser use (NO_3^-) and lack of wastewater treatment (NH_4^+) are common sources of nitrogen species finding their way into the water cycle in developing and newly-industrialised countries
- BF is regarded an efficient process for NO_3^- (denitrification under anoxic conditions) or NH_4^+ removal (nitrification under oxic conditions)
- High NH_4^+ levels in surface water are a major impairment to BF (<0.25 mg/L oxidised to nitrate in the presence of 1 mg/L O_2)

The element nitrogen is a nutrient to plants and animals, a major constituent for nucleic acids, proteins and chlorophyll. It can occur in seven oxidation states and transitions are often mediated via microbially-driven redox processes such as the dissimilatory nitrate reduction or mineralisation of organic nitrogen (N_{org}) to ammonium (NH_4^+). The two relevant microbially-driven processes affecting nitrogen turnover during bank filtration are:

- the oxidation of NH_4^+ via nitrite (NO_2^-) to nitrate (NO_3^-) under oxic conditions (nitrification) and
- the reduction of NO_3^- to gaseous nitrogen (N_2) under anoxic conditions (denitrification).

Nitrogen in its various forms dissolves easily in water. The occurrence of nitrate, nitrite and ammonium in aquifers is indicative for the prevailing redox conditions and allows for deductions on degradation efficiency of co-pollutants during bank filtration. The presence of nitrate and ammonium in groundwater can indicate an anthropogenic pollution (Höll, 2002). Spalding & Exner (1993) suggested that groundwater nitrate levels higher 20 mg/L may be interpreted as the result of human activities. Nitrogen isotope ratios ($^{15}\text{N}/^{14}\text{N}$) can supply information about the source and fate of nitrates and monitor travel times in the subsurface (Gates *et al.*, 2008).

The extensive use of N-fertilisers such as the highly soluble sodium nitrate (NaNO_3) or ammonium nitrate (NH_4NO_3), has led to a concentration increase in surface and groundwater. Agriculture, the food industry, combustion and industrial processes are just a few examples for human activities whereby nitrogenous compounds are released into the environment. Nitrogen is not per se considered hazardous but the excess of a nitrogen species can show adverse effects. This does not only include the acidification of rain, lakes, oceans and soil by the reaction of water and combustion by-products (nitrogen oxides) to nitric acid (HNO_3) but also the latter's function as fertiliser in water systems.

German drinking water regulations stipulate threshold values of 50 mg/L and 0.5 mg/L for nitrate and nitrite, respectively (TrinkwV, 2001). The WHO has recommended 50 mg/L as the maximum acceptable level for nitrate and a provisional guideline of 0.2 mg/L for nitrite under the assumption of long-term exposure. Particular attention is given to nitrite, the reduced form of nitrate, since it has been reported to impair the oxygen transport in blood and cause lethal methemoglobinemia in infants (Schuphan, 1974). Another health concern is constituted by the uptake of nitrate and its possible reaction with amines or amides, followed by the formation of carcinogenic nitrosamines in the human body (Vermeer *et al.*, 1998). In German drinking water guidelines, a threshold of 0.5 mg/L (30 mg/L for geogenic origin) applies for ammonia/ammonium ($\text{NH}_3/\text{NH}_4^+$), a cellular metabolite of nitrogenic compounds. Ammonia (as NH_3) which is toxic to fish, is volatile and only present at pH values >9. There is no WHO guideline value recommended.

In many countries nitrate in groundwater systems is a significant problem. Germany, for instance, has got a long history of N-fertiliser use. The EU Water Framework Directive (WRRL) set the goal to achieve a "good ecological state of water systems" by 2015 (EG WRRL, 2000). For groundwater systems, this "good state" comprises both quantity (balancing abstraction and replenishment) and quality (meeting guideline threshold values). In a country-wide investigation conducted in 2004, 980 groundwater reservoirs were analysed for contaminants (nitrate, pesticides, chloride, sulphate) and it was estimated that 48% will unlikely meet or fail the WRRL quality goals mainly due to elevated nitrate levels (UBA, 2005). In earlier investigations, out of 181 observation wells sampled between 2000 and 2002, 56% exhibited nitrate values >50 mg/L. However, there was a noticeable

trend for a nation-wide quality improvement in a ten-year observation period from 1992 to 2002 (Wolter, 2004). High nitrate levels in groundwater are also seen in developing or newly industrialised countries. In India, for instance, the concentrations were reported to exceed the permissible local threshold of 45 mg/L in 11 out of 28 states covering 95 districts (Kumar & Shah, *unknown*). In Jordan, 106 samples taken from 26 karst springs that were not even influenced by agriculture or industry but by untreated wastewater showed that 77% exceeded the Jordanian threshold of 20 mg/L. Still eight percent exceeded 50 mg/L (Obeidat *et al.*, 2008). These examples illustrate that nitrate is a common problem in surface and groundwater.

Nitrate is the predominant species under oxic conditions. Due to its negative charge, it is highly mobile within the solid-liquid phase (Obeidat *et al.*, 2008). Under anoxic conditions, nitrate is used as electron acceptor during dissimilatory nitrate reduction. Nitrate may either become reduced to NH_4^+ or to gaseous N_2 and N_2O (denitrification). The latter is commonly regarded the more important process since it gives a higher energy yield to microorganisms. The reduction of nitrate depends on the availability of electron donors (mainly organic matter) and mitigation of contaminated aquifers can take decades if conditions are unfavourable (Green *et al.*, 2008). Favourable conditions promoting denitrification without the drawbacks of a strongly reducing environment were suggested to be an organic carbon content of no more than 1-2% organic carbon in sediment and a flow velocity of several metres per day (Doussan & Joch, 1997). An example for denitrification was reported from a BF test site in Switzerland where surface water from the river Glatt exhibited 30 mg/L nitrate, concentrations in the aquifer near banks were between 5-10 mg/L and ammonium levels below 0.3 mg/L (Schwarzenbach *et al.*, 1983).

Nitrification, the oxidation of NH_4^+ to NO_3^- , is a temperature-dependent process. In winter time, ammonium may appear in abstraction wells due to decreased metabolism and sorption capacity in the subsurface (Michels & Schmidt, 1988). Doussan *et al.* (1998) suggested that alluvial and chalk sediments at an experimental bank filtration site in France retained NH_4^+ by sorption. They further reported that pore water in the top layers of the river bed sediments had NH_4^+ concentrations of 30 mg/L which was higher than in the anoxic groundwater environment below showing 20 mg/L NH_4^+ . This was believed to be the result of organic matter mineralisation by benthic microflora.

At a bank filtration site in India, Dash *et al.* (2008) compared monsoon and non-monsoon periods and observed that nitrate concentrations in lake water were in both seasons stable. The nitrate concentration found (~0.3 mg/L) can be considered as very low. Instead, ammonium was present in lake water which is rather uncommon in industrialised countries where sewage treatment is applied. Ammonium levels were found to be lower in monsoon (0.17 mg/L) than in non-monsoon periods (6.3 mg/L) which might be due to decreased dilution in the dry season. In both seasons, nitrate levels in bank filtrate increased from 0.2-0.3 mg/L to 3.5 mg/L which might be ascribed to

mineralisation of organic matter under oxic conditions. The bank filtrate share S_{BF} varied considerably from 80% during monsoon to 25-40% during non-monsoon periods.

Developing, newly-industrialised and industrialised countries are facing the same challenges in view of fertiliser use and the implications on groundwater systems. In order to prevent high nitrate levels in groundwater, fertiliser application should be regulated by law, alternatives such as organic fertiliser are to be considered, crop rotation applied and anthropogenic pollutions limited as far as possible. In some places, bank filtration may also be used to dilute ambient groundwater exhibiting elevated nitrate levels. Where precipitation extremes occur, variations in surface water (and thus, bank filtrate share S_{BF}) should be taken into consideration for final BF quality. Source water and groundwater can also exhibit extensive ammonium levels as result of anthropogenic pollution. This was observed during the TECHNEAU investigations at a site in Delhi (India) and was a major impairment for BF operation (Pekdeger *et al.*, 2008). In many developing countries, temperatures are more constant and not likely to interfere with nitrification as seen in winter months in Europe. However, in combination with high loads of organic carbon, higher temperatures may promote biodegradation whereby redox conditions can turn anoxic and impair the overall cleaning capacity of a BF site.

2.2.5.3 Phosphorus

- Phosphorus is not regarded as critical parameter for drinking water production by bank filtration but its distribution should be limited to avoid eutrophication of surface water bodies
- Removal of phosphate during BF occurs due to formation of insoluble species with Fe, Al and Ca. However, soil may serve as sink and source depending on ions present, concentration gradients, redox zones, temperature and pH

Phosphorus is commonly found in inorganic “phosphate rocks” (e.g. apatites) and due to its high reactivity, it never occurs as free element. It has the tendency to form insoluble minerals with metal and earth alkali ions. Thus, its bioavailability is low. In the form of phosphate-P, it is the third major nutrient. It is not only building material for cell membranes, and nucleic acids but in adenosinetriphosphate (ATP), phosphate is an important energy carrier for biochemical processes (Brock, 2000).

In natural waters, phosphate concentrations are about 0.1 mg/L and levels higher 0.3 mg/L in groundwater are considered indicative for anthropogenic pollution. The recommended phosphorus intake for adults is 700 mg/day, most of which is taken up via food. Concentrations <70 mg phosphorus/kg body weight per day are considered unobjectionable (USEPA, 2008).

A threshold for phosphate in German drinking water guidelines is not stated. Phosphate occurs in low concentrations in drinking water. Since it is only moderately bioavailable, it is the main limiting factor for growth of plants and algae. In surface waters, phosphate in abundance may promote algal production followed by bacterial decomposition of algae and oxygen depletion. This process called *eutrophication* may eventually result in fish die-off.

When the impact of excess phosphate on water systems was recognised, many countries restricted the use of detergents which was the primary source of contamination (Gilbert & DeJong, 1977). Phosphate originating from human excrements and detergents enters waterways via point-sources such as municipal effluent. In western industrialised countries, the main inlet is nowadays via diffuse sources like surface run-off and leaching from soil. Approximately, 90% of commercially used phosphorus is applied as fertiliser.

The mobility and sorption behaviour of phosphate in soil depends on various factors such as redox conditions, pH, temperature, hydraulic conditions, and presence of complexing ions as well as ion exchangers. In soils of neutral or alkaline pH, phosphate is retained well due to the formation of insoluble calcium, iron- or aluminium phosphates (Ziegler, 2001). In a study from China, phosphorus contents in lake sediments were shown to range from 217.8 to 1640 mg/kg of which inorganic phosphorus - bound to Ca, Al, Fe, Mn oxides and hydroxides (Fe/Al-P) - was the major fraction. Phosphate was mainly sorbed to Fe and Al particles and sorption capacity was stronger in eutrophic than in mesotrophic lake sediments (Wang *et al.*, 2005). In water treatment, Fe, Ca and Al-salts are also used as flocculants for the removal of phosphate.

Because of the precipitation with metals and cations which are abundant in the subsurface, bank filtration is generally considered efficient to remove phosphate (Schmidt *et al.*, 2003; Ziegler, 2001). However, experiments with soil columns demonstrated that soil may serve as sink or source for phosphorus (Mamo *et al.*, 2005). A study by Driescher *et al.* (1989) on the fate of phosphate during bank filtration conducted over a period of 8 years reported that there was no irreversible elimination of phosphate but smoothing of annual fluctuation extremes with a time lag of several months.

The over-fertilisation of soils at the expense of groundwater quality is a problem seen worldwide. For instance, Rajmohan & Elango (2005) found that 35% out of 43 wells sampled near the Pato and Cheyyar river basin in India in the years 1998/1999 were exceeding due to agricultural activities 0.54 mg/L phosphate, a former maximum limit suggested by the European Economic Community (Smeats & Amavis, 1981). Another study from India reported on excessive amounts of phosphate found in an eutrophic lake and the subsurface water below because the tributary river became polluted by phosphorite mining, industrial effluent discharge and sewage from settlements (Das, 1999). The success of bank filtration to supply high quality

drinking water will strongly depend on the efforts made by local governments to protect source water and decrease the nutrient load.

2.2.6 Anions and cations

- Anions and cations determine water taste, smell and odour influenced by aquifer material and geogenic/marine salinity without particular considerations for developing and newly-industrialised countries
- Most anions and cations are not removed by BF
- The aquifer matrix may serve as sink or source depending on ion exchange, pH and rock weathering

Groundwater chemistry is influenced by the water source and the interaction with the surrounding rock texture and is thus aquifer-specific. Höll (2002) grouped anions and cations that are found in groundwater into main water components (*typically* >10 mg/L), minor components (0.1-10 mg/L) and trace elements (<0.1 mg/L). Main components usually comprise the cations sodium (Na⁺), magnesium (Mg²⁺), calcium (Ca²⁺) and the anions chloride (Cl⁻), hydrogencarbonate (HCO₃⁻) and sulphate (SO₄⁻). Minor components are potassium (K⁺), manganese (Mn²⁺), iron (Fe²⁺), strontium (Sr²⁺) nitrate (NO₃⁻) and fluoride (F⁻). Many other elements are found in groundwater in traces including numerous heavy metals such as copper, lead and uranium. The components nitrate (NO₃⁻), nitrite (NO₂⁻), ammonia (NH₃) and phosphate (PO₄³⁻) are often indicators for an anthropogenic pollution of groundwater (Höll, 2002). Some of the anions and cations are also major nutrients (NO₃⁻, PO₄³⁻) and geogenic heavy metals (i.e. Mn²⁺, Fe²⁺) that are discussed in more detail in the respective chapters 2.2.5 (Nutrients) and 2.2.7 (Heavy metals). The factors influencing the concentration changes of anions and cations during bank filtration include mixing with ambient groundwater, ion exchange, precipitation/dissolution, sorption, complexation, redox reactions and microbial activities.

2.2.6.1 Cations: Na, Mg, Ca and K

The cations Na⁺, Mg²⁺, Ca²⁺ and K⁺ are required by living organisms to regulate their internal environment and maintain a stable condition. The content of mineral salts in drinking water determines the taste and constitutes a natural barrier for excess salt consumption. High salt concentrations may stress the water-electrolyte balance and kidney function. German drinking water regulations has set threshold values for electrical conductivity (EC) of 2500 µS/cm (at 20°C) and 200 mg/L for sodium. There are no guideline values recommended.

Aside from health aspects, a too high salt content is often unwanted for technical operation. During membrane filtration (as part of the water treatment process), mineral salts may cause membrane blocking (scaling) and subsequent fouling (Faurie & Boerlage, 2001). Water rich in sodium chloride also promotes metal corrosion. Calcium salts (and to a minor extent magnesium salts) are linked to the carbonate/carbonic acid equilibrium influencing pH buffering capacities and water hardness (Ch. 2.2.1

Temperature & pH). Water with low Ca^{2+} and Mg^{2+} concentrations (i.e. “soft” water) is preferable over “hard” water with high mineral content for distribution (e.g. network maintenance) and household applications (e.g. washing machines, dish washers etc.). When water is heated, for instance, calcite can precipitate from solution and form encrustations.

In calcareous aquifers, Ca^{2+} and bicarbonate concentrations can generally increase due to buffering of protons produced by organic carbon degradation. Groundwater is usually characterised by a higher amount of minerals because of natural weathering processes, thus, mineral levels often increase by mixing in BF production wells. Depending on the nature of the aquifer matrix, cation exchanger capacities (CEC) are more or less pronounced. All cations can be subject to ion exchange (if the system is not at steady state) or precipitate as insoluble compounds in the presence of suitable anions (if the system is not already saturated) (e.g. as calcium carbonate).

Shamrukh & Abdel-Wahab (2007) analysed mineral content in surface water, bank filtrate and ambient groundwater in Egypt and could thereby illustrate that mixing with mineral-rich, ambient groundwater had increased concentrations of calcium (+27%), magnesium (+29%) and potassium (+10%) in bank filtrate. At a lake bank filtration site in India, where the BF share (S_{BF}) in wells accounted for 80%, a strong increase (+108%) from 23.5 to 49 mg/L was observed after subsurface travel time of 1-2 days (Dash *et al.*, 2008). The TECHNEAU report 5.2.2 investigated inorganic substances and physicochemical parameters in surface and groundwater at bank filtration sites in Delhi, India (Pekdeger *et al.*, 2008). For a BF site, they showed the increase of Ca and Mg in shallow wells (4-9.5 m sampling depth) from 69 to 153 mg/L (+122%) and 28 to 40 mg/L (+43%) respectively. In middle-deep wells (7-13 m), levels were considerably lower and comparable to Yamuna river water exhibiting 69 mg/L for calcium and 21 mg/L magnesium.

2.2.6.2 Anions: Cl^- , NO_3^- , PO_4^{3-} , SO_4^{2-} and HCO_3^-

The anions Cl^- , NO_3^- , PO_4^{3-} , SO_4^{2-} and HCO_3^- are counterions of the aforementioned cations. Some minerals may dissolve easily in aqueous solutions but they can precipitate again as chlorides, carbonates, phosphates, nitrates or sulphates when ionic strength, pH, redox and temperature conditions change. In groundwater systems, the precipitation as nitrates is rarely observed.

Apart from naturally-occurring weathering processes, concentrations changes in groundwater can be of anthropogenic origin. This includes the infiltration of surface water or run-off influenced by municipal and industrial sewers (chlorides, sulphates) or the use of de-icing salt (chlorides) and fertilisers (nitrates, sulphates, phosphates). Chloride, sulphate and carbonate affect the taste of water in combination with calcium, magnesium and sodium (Ongerth *et al.*, 1964) and sulphate levels >150 mg/L have been suggested to result in noticeable taste. The threshold values set in German drinking water regulations are 250 and 240 mg/L for chloride and sulphate (500 mg/L, when

geochemically influenced) to prevent taste impairments and corrosion (TrinkwV, 2001). A threshold for PO_4^{3-} is not stated in present guidelines; whilst for nitrate a threshold of 50 mg/L applies to health considerations. Nitrate and phosphate are nutrients and discussed in the respective chapter (Ch. 2.2.7 Nutrients).

Chloride is non-reactive and therefore has often been used as tracer in BF systems (Sheets *et al.*, 2002). The only natural process that mitigates high Cl^- concentrations in groundwater is dilution. Bank filtration has been shown to reduce chloride concentrations found in Rhine water by dilution from 145 to 320 mg/L down to 100 to 160 mg/L. Rhine water traditionally carries high chloride levels because of salt-rich effluent discharged from potash mining works. In Egypt, the chloride concentration increased in bank filtrate because the ambient groundwater concentration was higher than in the infiltrating Nile water (Shamrukh & Abdel-Wahab, 2007). This is likely the case in coastal areas where groundwater may exhibit higher salinity.

Sulphate is another anion behaving rather conservative in BF systems (Schmidt *et al.*, 2003). However, a significant increase in sulphate (soluble) may be observed when oxygen-rich surface water enters a pyritic aquifer or reversely, under anaerobic conditions sulphate can become partially reduced by microorganisms to sulphide (Massmann *et al.*, 2003). Like nitrate, sulphate serves as electron acceptor where oxygen is unavailable but degradation kinetics in the absence of oxygen are usually slower (Schmidt *et al.*, 2003). Studies from India and Egypt observed an increase of SO_4^{2-} after subsurface passage, likely as the result of mixing with ambient groundwater (Dash *et al.*, 2008; Shamrukh & Abdel-Wahab, 2007).

Hydrogen carbonate or bicarbonate (HCO_3^-) can form by dissolution of carbonates or carbon dioxide in water or by microbial respiratory activities. It plays a major role in the carbonate-carbonic acid equilibrium (Ch. 2.2.1 Temperature & pH). The German drinking water regulations stipulate that water pH should not decline below the pH of calcium carbonate saturation when in contact with material prone to corrosion (e.g. concrete, metals). During bank filtration near the river Elbe in Germany, concentrations of carbonic acid were observed to increase from 0.13 in surface water to 0.31 mol/m³ in filtrate (Kühn & Müller, 2000). In the study by (Dash *et al.*, 2008), bicarbonate concentrations were seen to increase during subsurface passage between 1997 and 2006 on average from 225 mg/L in lake water to 308 mg/L (+37%) in filtrate during monsoon. The TECHNEAU report 5.2.2 (Pekdeger *et al.*, 2008) showed for the BF site in central Delhi, a significant increase in bicarbonate from 320 to 712 mg/L in shallow wells (4 to 9.5 m sampling depth) and slightly elevated concentrations of 392 mg/L in middle-deep wells (7-13 m sampling depth). The rise in bicarbonate after subsurface passage can be ascribed to mineralisation processes of organic matter under oxic conditions and production of carbonic dioxide.

Mixing is frequently the underlying reason for concentration shifts in bank filtrate, emphasising the need to know the quality of ambient groundwater.

The latter depends on the origin and genesis of groundwater and the extent of anthropogenic pollution. The above-mentioned anions and cations are natural components of water, most of which are tolerable even in higher quantities. When present in excess, they may impair water quality and require advanced post-treatment (e.g. reverse osmosis nanofiltration). Most major ions are not removed by bank filtration, but it has a certain capacity to dilute polluted surface water. There are no specific considerations for developing and newly-industrialised countries. The fate and influencing factors during BF is summarised in table 2.

Table 2: Fate of common cations and anions during bank filtration

Parameter	Fate during BF & influencing factors*
<i>cations</i>	
Na ⁺	ion exchange
Ca ²⁺	ion exchange, increase due to weathering
Mg ²⁺	ion exchange, increase due to weathering
K ⁺	ion exchange
NH ₄ ⁺	ion exchange, increase as product decay of organic matter, indicator for anthropogenic pollution, persistent under anoxic conditions
<i>anions</i>	
Cl ⁻	conservative, used as tracer in BF systems
SO ₄ ²⁻	rather conservative but significant increase possible when sulphidic aquifers become oxic and slight decrease under anoxic sulphate reduction
NO ₃ ⁻	>20 mg/L indicate anthropogenic influence transformed to N ₂ under suboxic/anoxic conditions
PO ₄ ³⁻	no irreversible elimination, smoothing of annual peaks potential decrease due to precipitation with metals and cations at pH >7 and microbial uptake,
HCO ₃ ⁻	increase due to mineralisation of organic matter and calcite/dolomite dissolution

*other than dilution

2.2.7 Heavy metals

- In some developing and newly-industrialised countries (e.g. Bangladesh, India, China), the burden of geogenic trace contaminants such as arsenic is particularly high, anthropogenic activities (mining and industrialisation) further release heavy metals into the environment
- The subsurface may serve as sink or source for heavy metals
- The presence of dissolved heavy metals (e.g. arsenic) may severely impair BF quality
- Heavy metals tend to sorb to positively-charged materials, e.g. Fe and Al (hydroxy-)oxides which occur predominantly under oxic conditions

It should be noted upfront that the term "heavy metal" has never been defined by any authoritative body such as the nomenclature surveilling "International Union of Pure and Applied Chemistry" (IUPAC). It has been used over the last six decades in different contexts grouping them by toxicity, density (>4.5 g/cm³) or other physicochemical concepts (Duffus, 2002). For sake of simplicity and with the focus placed on their toxic significance in water systems, herein all trace elements are denoted as heavy metals which do not belong to the more defined groups of alkali (earth) metals, noble gases and non-metals including hydrogen, the only exception being fluoride which is a halogen but also discussed in this chapter.

In the earth's crust, heavy metals are found in major concentrations in ores (i.e. as sulfides or oxides) or as components of other minerals, usually in trace concentrations. Several are essential trace elements to our diet (e.g. copper, zinc, selenium, chromium). Elevated concentrations, however, can show severe carcinogenic, teratogenic and mutagenic effects on the human body. The tendency of several heavy metals to bioaccumulate in bones (lead) and body tissue (cadmium, copper) puts especially infants at risk. Strictly speaking, all heavy metals are of geogenic origin but they will be distinguished herein into those predominantly entering the water cycle due to anthropogenic activities and those originating from the subsurface.

2.2.7.1 Primarily anthropogenic water pollutants: Pb, Cu, Zn and Cd

Heavy metals may enter the water cycle due to anthropogenic pollution sources such as mining, the metal-working industry, waste disposal, electroplating, combustion processes and many others. By committing the metal working industry to the implementation of effluent treatment, the discharge into German surface waters by point-pollution sources has been reduced substantially. Nowadays, diffuse pollution sources, i.e. the leaching from contaminated soils and rainwater run-off from metal-containing roofs (Cu, Zn, Pb), are more significant (Hillenbrand *et al.*, 2005). Heavy metals have largely been used as building material for water distribution networks

including lead (Pb), copper (Cu), cadmium (Cd), zinc (Zn), iron (Fe) and nickel (Ni). The two latter are water pollutants of frequently geogenic origin (Ch. 2.2.7.2 Geogenic water pollutants). Coatings of inert alloys are nowadays used at the water phase boundary to prevent corrosion and heavy metal leaching. In developing countries, but especially in newly-industrialised countries like China and India, mining, industrial discharge and emissions are major sources of pollution for heavy metals (Haiyan & Stuanes, 2003; Kar *et al.*, 2008). In the following, major primarily anthropogenic-derived water pollutants are briefly explained and the literature on their fate in the subsurface reviewed.

Lead (Pb)

Lead is a potent neurotoxin and bioaccumulant that is used in many applications such as in building construction, batteries, weights and fuels. It may accumulate in bones, teeth and brain tissue causing blood and brain disorders. In Europe, the major source of pollution was leaded fuel and until the mid-seventies, lead was a widely used building material in water pipes. Leaded fuel is still commonly used in Africa and large parts of Asia. German Drinking Water Guidelines set a threshold of 10 µg/l which is in accordance with the WHO guideline value (WHO, 2006; TrinkwV 2001). The presence of lead in waters is the result of human activities.

Bank filtration was shown to reduce lead by 75% from 12.6 to 3.2 µg/l (Schmidt *et al.*, 2003). However, Stuyfzand *et al.* (2006) found that during anoxic subsurface passage, the lead concentration first increased from 0.3 µg/l to 1.3 µg/l (after 10-100 m) and then decreased to 0.6 after 675 m demonstrating a potential for remobilisation.

Studies investigating the fate of lead in the subsurface reported that lead sorbs to sand and, fine silt particles as well as organic material (Colley, 1988; Miretzky *et al.*, 2007; Newman *et al.*, 1993). For instance, in slow sand filtration experiments, lead was shown to sorb well to sandy loam soil, supposedly due to complex formation with soil oxides and other components (Miretzky *et al.*, 2007). Christensen *et al.* (1999) found that in polluted groundwater influenced by landfill leachate, 85% of lead in solution were bound to DOC complexes. The sorption and complexation with colloids facilitates the migration of lead within the subsurface (Newman *et al.*, 1993). These findings suggest that removal of Pb during subsurface depends on the capacity of an aquifer to remove colloids and particles to which Pb is associated.

Cadmium (Cd)

Cadmium is toxic at low concentrations, a bioaccumulant in liver and kidney tissue that has been demonstrated to be carcinogenic, mutagenic and teratogenic to mammals. Cadmium is used in the steel-working industry, for plastics, batteries and fertilisers. Due to its high toxicity, a strict guideline

value of 3 µg/l and a threshold of 5 µg/l were set in the WHO and German drinking water guidelines respectively (TrinkwV, 2001; WHO, 2006).

For bank filtration, a removal efficiency of 75% has been reported by decreasing the concentration in surface water from 2 µg/l to 0.5 µg/l in bank filtrate (Schmidt *et al.*, 2003; Sontheimer, 1980). In the Netherlands, Cd levels were reduced during oxic passage from 14 µg/l to 10 µg/l in shallow aquifers (24 m, 4.5 d) and to <0.1 µg/l in middle deep aquifers (84 m, 18 d). At anoxic conditions, cadmium removal was slow from 0.03 µg/l to 0.01 µg/l within 1800 days. Bourg *et al.* (1989) found that Cd was easily co-dissolved with Fe and Mn oxides under only slightly oxidising conditions.

Pang *et al.* (2004) reported that retardation was positively correlated with pH and inversely related to flow velocity and metal concentration in column experiments. They found that large concentrations of bacteria can enhance mean transport velocity of colloid-associated cadmium up to 28 times. Also in column experiments, Dunnivant *et al.* (1992) observed a higher mobility in the presence of mobile DOC. Cadmium can sorb to iron(hydroxy)oxides and become remobilised by Fe dissolution under reducing conditions. It may also precipitate as sulphide under anaerobic conditions (Altmann & Bourg, 1997; Brand *et al.*, 1989). Groundwater pH and precipitation as otavite (CdCO₃) were suggested to considerably affect removal and retardation (Altmann & Bourg, 1997; Zahn & Seiler, 1992).

Thus, factors determining the retardation and mobility of cadmium in the subsurface were found to be pH and redox conditions, flow velocity, organic content, carbonates, colloids and metal concentration. Oxic and long bank filtration passage (long retention times) appeared to be advantageous for cadmium removal.

Copper (Cu)

Copper is an essential nutrient but also a drinking water contaminant that can cause fatigue, vomiting and inflammation when taken up in excess. Severe poisoning is rare but care should be taken by sensitive population segments, particularly infants. Copper is used as conductor and pipe material, for coinage, roofing and many other applications. The threshold value of 2 mg/L found in German drinking water regulations is in accordance with the WHO recommendation (TrinkwV, 2001; WHO, 2006).

During bank filtration, copper has been observed to be reduced by 77% from 31.8 µg/l to 7.5 µg/l (Schmidt *et al.*, 2003). Under anoxic conditions, copper levels fell within 10 m from 5 µg/l to <0.5 µg/l (Stuyfzand *et al.*, 2006).

Lin *et al.*, 2004 investigated heavy metal content and distribution in soil samples from active recharge basins in a wastewater reclamation plant. They reported that copper was preferentially associated with the oxide component in soil and that copper adsorption measured as k_d values correlated positively with pH values between 5 and 9 ($r^2 = 0.93$). Adsorption on Fe

oxides and precipitation as carbonate were further suggested to be major mechanisms of retention. Brand *et al.* (1989) also reported that Cu fixation in a carbonate dominated porous aquifer was determined by inorganic carbon content. Bourg *et al.* (1989) proposed that Cu mobilisation is linked to the mineralisation of organic matter to which Cu is sorbed. Christensen *et al.* (1999) found that in polluted groundwater influenced by landfill leachate, 85% of copper in solution were bound in DOC complexes.

Thus, factors influencing Cu removal during bank filtration are redox conditions and pH, sorption to ferric (hydroxy-)oxides, organic matter and precipitation as carbonate.

Zinc (Zn)

Zinc is an essential trace element commonly found in food and drinking water. The WHO regards 3 mg/L to be a potential impairment for water taste but no guideline value has been suggested, the main source of zinc being food. More common is zinc deficiency in developing countries affecting one third of the population in Southeast Asia and sub-Saharan Africa. However, free zinc ions in solution may be toxic to plants, invertebrates, and vertebrate fish. Zinc finds application in batteries, roofing, pipe material and the metal-working industry (e.g. in alloys).

Bank filtration has been shown to efficiently remove zinc after the first 10-15 m passage in bank sediment under anoxic conditions (Bourg & Bertin, 1993). It has been further observed near the river Rhine that zinc was reduced by 82% from 180 µg/l to 33 µg/l (Schmidt *et al.* 2003). Stuyfzand *et al.* (2006) reported removal from 26 µg/l to <5 µg/l within 10 m passage under anoxic conditions and from 40 µg/l to <10 µg/l within 84 m oxic passage. These studies suggest a good potential for zinc removal via bank filtration.

Sorption processes of zinc are influenced by pH and redox conditions, temperature, ionic strength, clay content, presence of sorbents such as ferrihydrites, Fe and Al (hydroxy-)oxides (Trivedi *et al.*, 2003; Casagrande *et al.*, 2004, Adhikari & Rattan, 2002). Zinc may precipitate as sulphide under anaerobic conditions and become remobilised when Fe and Mn (hydroxy-)oxides are solubilised. The findings suggest that even short infiltration paths (10 m) may be sufficient to retain zinc as long as conditions do not turn reductive for Fe(III)(hydroxy-)oxides.

Summary for anthropogenic heavy metals

The retention of heavy metals during subsurface passage is influenced by sorption, precipitation and ion exchanger processes which are dependent from pH and redox conditions, sediment texture, ionic strength and the nature of in/organic material present. Oxic conditions appear to be more

suitable for removal due to the immobilisation of hydroxy(oxides) to which heavy metals sorb.

Table 3: Heavy metals of anthropogenic origin during bank filtration

parameter	fate during BF & influencing factors
Pb	<p>removal observed: 75% high affinity to sorb to colloids, fine sands, clay, organic matter and building complexes remobilisation possible, closely linked to the fate of particles/colloids during subsurface passage</p>
Cd	<p>removal observed: 29-99% depends on pH, redox potential, flow velocity, sorption to colloids (bacteria) and organic matter; organic matter may enhance Cd mobility; potential precipitation as carbonate and sulphide under anaerobic conditions remobilisation possible when Fe (hydroxy-)oxides become dissolved under anoxic conditions</p>
Cu	<p>removal observed: 77-90% depends on pH, redox potential, sorption to organic material, Fe (hydroxy-)oxides, precipitates with carbonates and sulphides (under anaerobic conditions), sorption/desorption and precipitation/dissolution reactions are major factors for retardation, remobilisation possible, pH changes due to mineralisation of organic matter under oxic conditions, remobilisation when Fe (hydroxy-)oxides become dissolved under anoxic conditions</p>
Zn	<p>removal observed: 75-82% good removal capacities suggested for BF (within 10 m), depends on pH, redox potential, temperature, ionic strength, sorption to clay, Fe & Al (hydroxy-)oxides, ferrihydrite potential precipitation as sulphide under anaerobic conditions remobilisation possible, remobilisation when Fe (hydroxy-)oxides become dissolved under anoxic conditions</p>

Developing and newly-industrialised countries in particular face problems with heavy metal pollution since economic goals obtain priority over environmental and health considerations (Mohan *et al.*, 1998). Leaded fuels, for instance, are still commonly used in Africa and large parts of Asia. The spreading of anthropogenic pollutants into the water cycle may be controlled by source water protection and emission legislation. This is in contrast to geogenic pollutants in groundwater that may remain undetected until water

abstraction alters redox conditions and mobilises them into the water phase. In the following table 3, the potential removal of anthropogenic pollutants by BF and influencing factors in the subsurface are summarised.

2.2.7.2 *Primarily geogenic water pollutants: As, F, Fe, Mn, Se, Cr, U*

Several trace elements including arsenic (As), fluoride (F), selenium (Se), chromium (Cr), manganese (Mn), iron (Fe) and nickel (Ni) may occur naturally in concentrations impairing groundwater quality. Such impairments can be health-relevant (As, F, Se, Ni) or be of aesthetical relevance (Fe, Mn). Groundwater abstraction can trigger the remobilisation by changing redox conditions. Approximations for the removal of unwanted trace elements during bank filtration do require a thorough understanding of the aquifer characteristics and ideally experimental data whether an aquifer serves as sink or source for pollutants.

Arsenic (As)

Arsenic is an element occurring throughout the earth's crust in combination with oxygen, chlorine and sulphur, particularly in copper or lead containing minerals and (iron) ores. Thus, arsenic in groundwater is mostly of geogenic origin and the result of dissolved minerals from weathered rocks and soils (Brooks & Virta, 2005). However, there are also man-made sources such as agricultural applications, disposal of arsenic-containing waste, mining and smelting processes.

Arsenic is responsible for one of the world's biggest case of mass poisoning. In the 1970's, the WHO drilled millions of shallow wells into the Ganges delta in Bangladesh remobilising arsenic into the water phase. In Bangladesh alone, about 40 million people are nowadays exposed to unhealthy arsenic levels either indirectly via crop irrigation or directly via consumption of arsenic-contaminated well water. Due to bioaccumulation within the body, consumers are at risk of diseases related to chronic arsenic poisoning such as cancer and arsenicosis (Saha *et al.*, 1999). More than 40 major incidents of groundwater arsenic contamination have been reported round the world (e.g. Bangladesh, India, Thailand, Chile, Mexico and the USA). It is estimated that approx. 137 million people in 70 countries are drinking contaminated groundwater with As levels exceeding the WHO guideline value of 10 µg/l. The German threshold value corresponds to the WHO guideline value (TrinkwV, 2001; WHO, 2006).

The underlying cause for the arsenic epidemic in Bangladesh is not entirely understood. In the environment, the two inorganic forms of arsenic are arsenite As (III) and arsenate As (V), both strongly sorb to iron(III)hydroxides. The introduction of oxygen by extensive water abstraction has been suggested to have oxidised pyrite-bound As (Höll, 2002). Other proposed that under the anoxic conditions that follow aerobic degradation, Fe(III)(hydroxy-)oxides are microbially reduced to siderite

(FeCO₃) in conjunction with reduction of As (V), whereby the toxic As (III) becomes remobilised (Jönsson & Sherman, 2007).

Nonetheless, also the function of soil as sink has been described in literature. In a 3-year-period removal by 93% from 4.2 µg/l in surface water to 0.3 µg/l in bank filtrate from the river Rhine has been reported (Schmidt *et al.*, 2003). Stuyfzand *et al.* (2006) observed fluctuations during anoxic subsurface passage in the Netherlands. Starting concentrations of 2 µg/l in surface water fell below 1 µg/l after 100 m and rose again to 1.5 µg/l after 675 m subsurface passage. After 25 m passage through a shallow, oxic aquifer, As levels of 1.5 µg/l were more than halved down to 0.6 µg/l.

Depending on redox conditions and the presence of complex building compounds (e.g. pyrite), arsenic can either be removed from the water phase or mobilised during bank filtration. Findings from a study based on the investigation of 46 private wells in the United States further suggested that arsenic in the water phase correlated positively with pH (i.e. threshold values were exceeded where pH ≥ 8) and reversely correlated with the presence of organic material and dissolved oxygen (Senior & Sloto, 2006).

Arsenic can readily change valence states and react to species of varying toxicity and mobility (arsenite>arsenate). When planning bank filtration schemes, the geochemistry at the site should be investigated; otherwise there is a risk that bank filtrate quality becomes deteriorated by arsenic mobilisation during subsurface passage. Some developing and newly-industrialised countries such as India and Bangladesh are countries plagued with contaminants of geogenic origin (e.g. As, F), a situation which is further aggravated by malnutrition and lack of financial means to ease the problem (Ayooob & Gupta, 2006). The TECHNEAU studies carried out in Delhi (India) found at one BF field site arsenic levels exceeding German drinking water standards affirming the need for prior investigations (Pekdeger *et al.*, 2008).

Fluoride (F)

Fluoride is a halogen and essential trace element to the human diet but toxic at higher concentrations. Chronic fluoride poisoning can result in tooth mottling, damaged joints and bone deformities (fluorosis). At low concentrations, however, it has been recommended to be used in dental care products since it is deemed beneficial against tooth decay (WHO, 2006). The threshold value of 1.5 mg/L found in German drinking water regulations is in accordance with the guideline value recommended by the WHO (TrinkwV, 2001; WHO, 2006). In India, fluorosis ranks first as the most spread geochemical disease affecting more than 66 million people of which 6 million are children under age of 14. An estimated 200 million suffer from fluorosis in 25 nations worldwide. Severely affected are the two most populous countries in the world, India and China.

At two bank filtration sites in the Netherlands, Stuyfzand *et al.* (2006) investigated the hydrochemistry. One BF site was characterised by oxic subsurface travel (84 m, 18 days) and the other one by anoxic/anaerobic conditions (675 m, 2900 days). Fluoride concentrations were slightly reduced during oxic passage starting from 0.2 mg/L in surface water and falling down to 0.07 mg/L after 84 m passage. At the anoxic site, where oxygen and nitrate were reduced after 10 m infiltration and iron-reducing conditions prevailed, manganese and iron levels were found increased. In this well, the fluoride concentration nearly doubled from 0.15 mg/L to 0.28 mg/L which was still seen after 220 m subsurface passage. At the monitoring well in 675 m distance to the bank, levels had decreased again to 0.08 mg/L. For a bank filtration site in India, the Techneau report 5.2.2 demonstrated mean levels of 2.6 mg/L in the Yamuna river, falling down to 1.8 mg/L (with large fluctuations between 5 mg/L and below detection limit) in shallow well water (4-9.5 m) and then rising up to 3.4 mg/L in middle-deep well water (31-37 m) (Pekdeger *et al.*, 2008).

Fluoride-rich groundwater in India has been described to coincide with low calcium and high bicarbonate concentrations (Ayoob & Gupta, 2006). Fluoride may precipitate as insoluble CaF₂ under neutral pH conditions. Sorption of fluorides has been reported to strongly correlate with the presence of Al and Fe where these elements occur as high-surface-area amorphous, oxide phases. Complexation via ligand exchange with surficial hydroxyl groups is deemed the dominant sorption mechanism to aluminium sulphate (Harrington *et al.*, 2003). Thus, fluoride levels are sensitive to pH and redox conditions affecting sorption processes, dissolution and precipitation.

Iron (Fe) and Manganese (Mn)

Iron is often mentioned along with manganese since both are essential trace elements, belonging to the most abundant elements in the earth's crust and usually occur together. Elevated concentrations of dissolved manganese and iron compounds can impart an objectionable taste, smell and colour to water. German drinking water regulations stipulate a threshold of 0.05 mg/L and 0.2 mg/L for manganese and iron respectively which were set to control aesthetic water quality and limit encrustations in the distribution network. A guideline value of 0.4 mg/L has been proposed for manganese by the WHO, no guideline for iron has been recommended (WHO, 2006).

In terms of health, manganese is considered as one of the least toxic elements upon oral uptake. Reports of adverse health effects are limited to cases of severe poisoning. A study from Japan reported symptoms including lethargy, increased muscle tone, tremor and mental disturbances after consuming water that contained 28 mg/L of Mn from a well influenced by 400 nearby buried dry-cell batteries (Kawamura *et al.*, 1941). Manganese is used in iron and steel alloy manufacturing, in batteries, glass, fireworks and fertilisers (WHO, 2006). Iron is an indispensable material in the metal-working and steel industry accounting for 95% of worldwide metal production (WHO, 2006). A

possibly lethal dose of excess iron was reported to be >40 mg/kg body weight and autopsies of bodies subject to iron intoxication revealed haemorrhagic necrosis and stomach mucosa sloughing off. Both, manganese and iron intoxication is quite uncommon.

Both elements occur naturally in soils, and in water that is in contact with these soils. The divalent forms of Fe and Mn are well soluble and occur only in the absence of oxygen and nitrate. Under oxic conditions, they are oxidised to Fe (III) and Mn (III/IV) and precipitate as (hydroxy-)oxides (Martin, 2005). Under strictly anaerobic conditions, they may precipitate as sulphides as the result of microbial sulphate reduction. Iron (II) and manganese (II) may serve as electron source to iron- and manganese-oxidising bacteria in soil. Reversely, in the absence of O₂ and NO₃⁻, iron (III) and manganese (III/IV) can be used as electron acceptor for carbon degradation whereby they become reduced and remobilised into the water phase (McMahon & Chapelle, 2008; Weber *et al.*, 2006).

Their occurrence as dissolved ions or minerals depends on redox potential, anions present, pH and metabolic activity by soil microorganisms. Iron and manganese from infiltrating surface water are retained during subsurface passage (Agerstrand, 1982; Schöttler, 1986) when redox conditions allow for precipitation and complexation processes with organic content in soil. In the subsurface, heavy metals often adsorb onto Fe and Mn oxide surfaces or become incorporated into Fe and Mn matrices as impurities (Martin, 2005). However, in anoxic and anaerobic groundwater from abstraction wells, elevated levels of dissolved Mn (II) and Fe (II) are commonly found and may then impair water quality as described above.

Bank filtration is unsuitable to remove Fe and Mn. Both are ubiquitously present in groundwater systems and become increasingly dissolved in the absence of oxygen and nitrate until redox conditions turn sulphidic. Under sulphate-reducing conditions, they may precipitate as sulphides. Redox conditions are the major factor determining whether bank filtration requires post-treatment for Fe and Mn removal. It is presumed that redox conditions in developing and newly-industrialised countries tend to more anoxic and anaerobic conditions. This is due to warmer temperatures and strong oxygen depletion following biodegradation when organic-rich water infiltrates. Thus, elevated Fe and Mn levels in abstracted well water seem likely in those regions. Manganese and iron concentrations can easily be reduced by common treatment methods including aeration and filtration.

Nickel (Ni)

Nickel has been demonstrated to be an essential nutrient to plants and some microorganisms. It finds application in the production of stainless steel, pipe material and nickel alloys. Contamination can arise from waste disposal leaching, industrial spills and in some cases from natural weathering processes (Larsen & Postma, 1997). Nickel may occur associated with

different rocks such as schist, sandstone and mudstone. It is an allergen in contact with skin and carcinogenic upon inhalation but its carcinogenic effect after oral uptake has not been evidenced (WHO, 2006). The German drinking water regulations set a threshold of 0.02 mg/L for Ni which is stricter than the guideline value of 0.07 mg/L recommended by the WHO (TrinkwV, 2001; WHO, 2006).

Nickel has been reported to be removed by 51% from 9.5 to 4.7 µg/l during bank filtration (Schmidt *et al.*, 2003). After 10 m of anoxic subsurface passage, 3.3 µg/l of nickel were observed to be reduced by 85 % to 0.5 µg/l. During oxic passage, levels had slightly increased from 1.5 µg/l to 1.7 µg/l after 35 m (Stuyfzand *et al.*, 2006).

The most prevalent oxidation state in compounds is Ni (II) which has the tendency to build complexes such as soluble hydrocomplexes in water. In Germany, increased levels of Ni have been observed in groundwater systems that are poor in carbonate (Cremer, 2002). Larsen & Postma (1997) reported that in such aquifers the buffering capacity and thus, the pH, is low and can cause nickel dissolution. Belova *et al.* (2008) suggested that sorption onto chalk (>90% calcite) significantly decreases Ni mobility but under conditions of calcite dissolution (pH <6), it becomes remobilised. Cremer (2002) compared shallow and deep aquifers with regard to nickel dissolution. Groundwater in shallow aquifer that was close to surface water was found to be low in pH. The increase in nickel has been ascribed to low pH and desorption of nickel from clay minerals and Fe(hydroxyl-)oxide surfaces. In deep aquifers, however, changing redox conditions were considered to be the cause for nickel remobilisation. Pyrite oxidation and dissolution of nickel carbonates due to acidification by precipitation of Fe(III)(hydroxy-)oxides were identified as the main processes in 50 to 70 depth (Cremer, 2002). At anaerobic conditions, nickel may precipitate as sulphide.

For removal efficiency of nickel during bank filtration, it may be concluded that anoxic conditions which are not yet iron-reducing are most suitable. Furthermore, calciferous aquifers are advantageous for pH buffering to prevent dissolution of nickel-containing minerals and precipitation of Ni carbonates. There is no particular consideration for developing and newly industrialised countries reflected in literature.

Selenium (Se)

Selenium is an essential trace element and bioaccumulant which can - depending on the dose and time of exposure - cause a range of intoxication symptoms including fatigue, irritability, hair and fingernail changes up to more severe damages of the peripheral nervous system, kidney and liver tissue. Selenium is found in the earth's crust where it is often associated with sulphurous minerals. As a micronutrient, it is taken up by plants and has even been suggested to be a natural antidote to arsenic poisoning (Spallholz *et al.*, 2008). Anthropogenic activities such as combustion of fossil fuels, mining

and the metal-working industry release selenium compounds into the environment. For drinking water, the WHO suggests a threshold value of 10 µg/litre which is in line with German drinking water regulations (TrinkwV, 2001; WHO, 2006). For some regions in China, selenium levels between 50 and 160 µg/l have been reported (Höll, 2002). At pH extremes, especially at alkaline conditions, concentrations in water can be elevated. The soluble species selenite, selenate, selenocysteine, and selenomethionine are also the ones deemed toxic (WHO, 2006). However, except than in certain seleniferous areas, selenium concentrations usually do not exceed the WHO guideline.

There is little information available on the fate of selenium during bank filtration. It has been reported that selenate Se (VI) is found in oxic/suboxic groundwater and selenite Se (IV) levels rise with increasingly anoxic, Fe-reducing conditions. Selenite may form crystals (e.g. selenite gypsum) in the presence of brines. Organic selenide Se (-II) was likewise found under anoxic conditions and pH-induced desorption of Se (VI) from aquifer material has been suggested (Basu *et al.*, 2007). Se (VI) may become reduced and immobilised by dissimilatory reduction to selenium Se (0). This was also seen during slow sand filtration simulation (Carlo *et al.*, 1992) and in experiments using “biobarrier” columns (Hunter & Kuykendall, 2005). Hunter & Kuykendall (2005) reported that 98% removal of selenite-Se (initial conc.: 10 mg/L) was removed within 4 weeks after circulation through columns, half of which was reduced to selenium. The columns had been fed with vegetable oil as C-source to establish a biologically-active layer.

Bank filtration may have potential to remove selenium; however, sorption processes are reversible depending on pH and redox conditions. Microbial turnover of selenate/selenite to selenium can - if not limited by nutrients - contribute significantly to their immobilisation. There was no indication in the reviewed literature that seleniferous areas are more common in developing countries or newly-industrialised than in industrialised countries.

Chromium (Cr)

Chromium and chromium salts are present in the earth's crust and widely used in industrial applications including manufacturing of catalysts, paints, leather, fungicides as well as ceramic/glass production and photography (WHO, 2006). Like selenium, chromium is deemed an essential trace element to our diet and is known to act harmful at high concentrations, especially upon inhalation. Consumption of water contaminated with hexavalent chromium has been linked to stomach cancer in China (Beaumont *et al.*, 2008). Generally, concentrations in groundwater are low (<1 µg/l), however, there are local exceptions. For instance, in the alluvial aquifers of the Californian Mojave Desert, the chromium concentrations in alkaline, oxic groundwaters exceeded the WHO guideline value of 5 µg/l (Izbicki *et al.*, 2008; WHO, 2006). This value which is provisional due to uncertainties concerning chromium toxicity upon oral consumption is also the threshold value in German drinking water regulations (TrinkwV, 2001; WHO, 2006).

The soluble hexavalent chromium Cr (VI) is deemed toxic and carcinogenic. It may occur as chromate (CrO_4^{2-}) or bichromate (HCrO_4). Minerals containing chromate are soluble, very mobile and poorly retained by aquifer minerals due to their negative charge. The trivalent species Cr (III) is relatively low in toxicity. It is the most prevalent species in soil and immobile under moderately alkaline to slightly acidic conditions (Palmer & Puls, 1994). Chromium removal strategies usually include a reduction step to the rather insoluble Cr (III). In contact with organic matter and ferrous minerals, Cr (VI) is easily reduced to Cr (III) forming hydroxides and complexes. Microbial sulphate-reducers have also been reported to reduce Cr (VI) to Cr (III). Thus, the distribution of chromium species varies with redox conditions, pH, kinetics, organic content and microflora present.

At a bank filtration site near the river Rhine, among the 12 heavy metals investigated, chromium was removed best from 7.9 $\mu\text{g}/\text{l}$ down to 0.5 $\mu\text{g}/\text{l}$ (-94%) after subsurface passage (Schmidt *et al.*, 2003). In the Netherlands, reduction of chromium in the first 10 m of (mostly anoxic) subsurface passage from 4 $\mu\text{g}/\text{l}$ down to <0.5 $\mu\text{g}/\text{l}$ was observed (Stuyfzand *et al.*, 2006). These findings suggest that bank filtration holds potential to reduce chromium, however, possible reductants in the aquifer should be identified and the reduction capacity evaluated (Palmer & Puls, 1994).

Chromium levels in surface waters are linked to the extent of industrial activity and may augment the usually low concentrations in groundwater. Other than for arsenic, a tendency for a higher burden of geogenic chromium in developing and newly-industrialised countries is not reflected by the reviewed literature.

Uranium (U)

Out of all naturally occurring elements, uranium has the highest atomic weight. It occurs in low concentrations (a few ppb) in soil, rock and water and is weakly radioactive. Uranium is mined and exported for military purpose and nuclear energy application by several countries (e.g. Australia, Canada, the United States, Russia, South Africa, Niger). Uranium concentrations in the water cycle may derive from mining activities, the operation of nuclear power stations, the use of phosphate fertiliser containing uranium or be of geogenic origin.

Uranium was shown in animal experiments to be highly toxic affecting inner organs, i.e. kidneys and liver. In order to address the naturally elevated uranium concentrations in some German groundwaters, a threshold of 10 $\mu\text{g}/\text{l}$ has been suggested by the Federal Environmental Protection Agency (Konietzka *et al.*, 2005). A guideline value of 15 $\mu\text{g}/\text{l}$ has been proposed by the WHO (WHO, 2006). In surface water, concentrations may range from 0.03 $\mu\text{g}/\text{l}$ (Amazonas River) to 3.9 $\mu\text{g}/\text{l}$ (Ganges River) (Merkel, 2002). Whilst in Germany, surface water levels vary between 1 and 3 $\mu\text{g}/\text{l}$, groundwater has been shown to exhibit concentrations between 1 to 100 $\mu\text{g}/\text{l}$.

Naturally occurring uranium in groundwater is usually a result of uranium dissolution from crystalline bedrocks such as granite (Babu *et al.*, 2008). Since hexavalent uranium is soluble at neutral pH, it is ubiquitous in the hydrosphere. It does form soluble complexes with inorganic (e.g. carbonate complexes) and organic ligands (e.g. oxalate, citrate). Levels were observed to be elevated in aquifers with high organic content or adjacent to marshland (Lindenthal, 2006). Furthermore, solubility is high under oxic conditions. Uranium can become reduced to uranium (IV) and precipitate as oxide (e.g. as uraninite). Uranium is primarily reduced by sulfate reducers (Abdelouas *et al.*, 2000).

There is little information in literature on the fate of uranium during bank filtration but oxic conditions and carbonates present seem not to impair solubility. The literature reviewed suggests that with regard to low concentrations in surface water and no indication for mobilisation potential under BF conditions, ambient groundwater can be seen as a primary source for uranium. Developing and newly-industrialised countries are not found to be particularly burdened with high levels of uranium in groundwater systems.

Summary for geogenic heavy metals

Heavy metals have been reported to be potentially removed during bank filtration by sorption and precipitation processes. Removal efficiency at a bank filtration site in Germany varied for different elements between 0 and 94% in a 3-year-period (Schmidt *et al.*, 2003).

A particular problem are geogenic heavy metals since they may deteriorate bank filtrate during subsurface passage and are more difficult to control than heavy metals infiltrating with surface water. Whether they become mobilised or immobilised depends largely on redox conditions, pH, the presence of suitable sorbents and counterions for precipitation.

Under aerobic conditions, heavy metals can sorb to surfaces exhibiting a negative charge (e.g. clay minerals, ferric oxides, organic solid matter) whilst anoxic conditions can lead to reductive dissolution of Fe(hydroxy-)oxides and thus, remobilisation of heavy metals. Under strictly anaerobic conditions, heavy metals may precipitate as sulphides (Schöttler, 1986; Ziegler, 2001; Schmidt *et al.*, 2003; Förstner, 1995). In table 4, an overview of geogenic pollutants, their potential fate during bank filtration and their importance (i.e. documented prevalence) for developing and newly-industrialised countries is provided.

Table 4: Heavy metals of geogenic origin during bank filtration

Parameter	Fate during BF	Importance & prevalence for developing and newly industrialised countries
As	<p>Oxic: BF holds potential for removal (93% reported), strong sorption to Fe (hydroxy-)oxides</p> <p>Anoxic/anaerobic: remobilisation by dissolution of ferric-bound As</p>	Important (137 million at risk for arsenicosis in 70 countries, primarily India & Bangladesh)
F	<p>Oxic: sorbs to Al and Fe present in high-surface-area amorphous and crystalline oxide phases</p> <p>precipitation as CaF</p> <p>Anoxic/anaerobic: remobilisation by dissolution of Fe and Al bound arsenic</p> <p>precipitation as CaF</p>	Important (200 million suffer from fluorosis in 25 countries, primarily India & China)
Fe & Mn	<p>Oxic: insoluble as (hydroxy-) oxides & carbonates</p> <p>Anoxic/anaerobic: Remobilisation of divalent Fe(II) and Mn (II) ions, possible precipitation as sulphides under sulphate-reducing conditions</p>	Important worldwide
Ni	<p>Oxic: mineralisation of organic matter may decrease pH, desorb Ni from clay minerals and Fe (hydroxy-) oxides</p> <p>Anoxic/anaerobic: dissolution of Fe minerals and carbonates mobilises Ni, precipitation of NiS under anaerobic conditions</p>	Moderately important
Se	<p>Oxic: soluble as Se (IV) and Se (VI)</p> <p>Anoxic/anaerobic: Dissimilatory reduction to Se (0) possible</p>	Moderately important
Cr	<p>Oxic: Cr (VI) is soluble and mobile, poorly retained by negatively-charged aquifer</p>	Moderately important

Parameter	Fate during BF	Importance & prevalence for developing and newly industrialised countries
	minerals Anoxic/anaerobic: potential for removal when reduced to less toxic Cr (III) presence of reductants (e.g. organic material, Fe minerals) necessary or sulphate-reducing bacteria	
U	Oxic: forms soluble complexes with inorganic and organic ligands as U (VI) Anoxic/anaerobic: reduced to U (IV) and immobilised, often by sulphate reducers	Moderately important

Potential of BF to attenuate heavy metal pollution in developing and newly-industrialised countries

The contamination of water sources with inorganic trace elements must be regarded a considerable problem in developing and newly industrialised countries. This is partly due to naturally high concentrations of geogenic trace elements in the subsoil (e.g. arsenic, fluoride), but also to the presence of mineral resources followed by mining-related pollution and indiscriminate industrial growth at the expense of the environment, often lacking waste water and water treatment.

Bank filtration is a valuable treatment tool where the geogenic burden of heavy metals is low and no costly post-treatment of abstracted bank filtrate is necessary. In aquifers with long travel distances and ambient groundwater with low heavy metal concentrations present to dilute infiltrating surface water, high loads from surface water can be reduced. Due to their tendency to be associated with colloids and particles (e.g. suspended solids), their retention is also influenced by the capacity of a BF system to remove particulate matter. The mobility of heavy metals during BF strongly depends on redox conditions. Under oxic conditions, they sorb onto Fe and Al (hydroxy-)oxides and become removed from the water phase. Under anoxic, Fe-reducing conditions, (hydroxy-)oxides dissolve and heavy metals (e.g. As, Fe, Mn etc.) are mobilised into the water phase. When conditions turn sulphate-reducing (anaerobic), heavy metals may precipitate as sulphides. Apart from redox conditions, the leaching potential for heavy metals is further influenced by pH, content of organic matter and the nature of the aquifer material (e.g. calciferous rock). Prior to the implementation of BF, parameters should be studied to assess the potential for heavy metal removal or mobilisation.

2.2.8 Organic micropollutants

The term organic micropollutants covers a wide range of organic substances that are found in the aquatic and terrestrial environment due to man-made activities and pollution. They may enter the water cycle via diffuse and/or point sources and show cumulative and synergistic adverse effects on human health. Some have been observed to be readily degradable while others are persistent. The same is true for the degradation products and sometimes the toxicity of a metabolite is even higher than of the parent compound (e.g. vinyl chloride is more toxic than 1,2-dichloroethene).

The following subchapters cover organic chemicals of major concern to groundwater abstracted drinking water including pesticides, aromatic hydrocarbons and chlorinated hydrocarbons as well as emerging groups of concern such as pharmaceuticals, endocrine disruptors and disinfection by-products for which to date the health implications are not fully understood. The list of micropollutants discussed is not exhaustive and the classification of substances may sometimes overlap. Several organochlorine pesticides, for instance, have been recognised to be potent endocrine disrupting compounds.

Industrial growth and changed land use practices (e.g. synthetic fertiliser use) have spurred the production and release of myriads of micropollutants into the environment and thus, the hydrosphere. In groundwater systems, loads of organic micropollutants may attenuate becoming subject to dissolution, advection, dispersion, diffusion, sorption, volatilisation and degradation processes. This chapter aims at assessing the risk posed by organic pollutants and the potential for attenuation during bank filtration.

2.2.8.1 Pesticides

- Pesticides are an issue in developing and newly-industrialised countries due to increased pesticide production and application which is seen alongside mishandling and lack of precaution, water source protection or quality monitoring
- Degradation by BF is specific for redox conditions and the substance as can be seen in the large variance of degradability observed, sorption is promoted by moderately-to-high organic matter and clay content
- Seasonal shock loads from surface run-off are mitigated

Pesticides are substances toxic to pests such as insects (insecticides), plants (herbicides) and fungi (fungicides). They are utilised in many applications in households and agriculture, from where they find their way into the water cycle (Miller, 2004). This includes **herbicides** like mecoprop, dichlorprop and atrazine, **fungicides** like dicloran or **insecticides** such as diethyltoluamide (DEET), primicarb and dichloro-diphenyl-dichloroethane (DDT).

Several pesticides have been banned from commercial use after their adverse effect on human and animal life has been recognised. Little is known about the risk constituted by pesticide mixtures as studies usually focus on single compounds.

Organochlorine pesticides such as the fungicide vinclozoline constitute a major concern acting as endocrine disruptor, vinclozoline was also shown to be mutagenic in rats. The insecticide DDT that causes reproductive ailments in birds and was suspected (though not evidenced) to be carcinogenic in humans was banned by most countries in the 1970's. Nowadays, DDT is produced and exported by India and China only. India, however, restricts the use to malaria control and limits the production to 10,000 tons per annum (Dash *et al.*, 2007).



Fig. 3: Agricultural use and pesticide application compromise groundwater quality

The “Pesticide Manual” lists 1,524 different pesticides (BCPC, 2008), the EU guideline 91/414/EG considered 1,150 different substances for accreditation and Greenpeace commissioned a study in which the toxicity of 1,134 pesticides was evaluated (Neumeister & Reuter, 2008). In Germany alone, 245 pesticides are permitted for use (Sturm & Kiefer, 2007).

German drinking water regulations stipulate concentrations lower than 0.1 µg/l and 0.5 µg/l for single pesticides and the sum of pesticides respectively for drinking water. However, individual thresholds apply for critical pesticides e.g. 0.03 µg/l for aldrine/dieldrine, heptachlor and heptachlorepoxyde (TrinkwV, 2001). There are also WHO guideline value recommendations for individual pesticides ranging from 0.03 µg/l for aldrine/dieldrine to 100 µg/l for dichlorpop (WHO, 2006).

A survey was conducted by the DVGW among water suppliers to collect data on pesticides in ground- and surface water between 2000 and 2006 (Sturm & Kiefer, 2007). It revealed that 182 participating companies (out of 1.500 asked) had detected pesticides in source water, half of which belonged to the group of illegal or meanwhile banned pesticides. This result confirmed an earlier DVGW study from 1994 where 183 (out of 1.450 asked) reported positive findings with 60% of the substances being meanwhile banned (Skark & Zullei-Seibert, 1999). The pesticides banned are commonly organochlorines such as chlordane, DDT, aldrine/dieldrine, endrine, heptachlor or lindane. These findings suggest a long-term persistence of pesticides in the subsurface.

Surface water can become polluted by diffuse such as agricultural run-off or point-sources such as wastewater effluent (Gerecke *et al.*, 2002; Neumann, 2002). Mathys (1994) examined the degree of pesticide pollution in an agricultural area based on data collected from surface and groundwater bodies between 1987 and 1992. The observation wells influenced by bank filtrate accounted for significantly higher pesticide levels than ambient groundwater wells.

Moncrieff *et al.* (2008) investigated the transport of organochlorine pesticides from surface water to groundwater in Nicaragua. One of the rivers studied exhibited a considerable difference in pesticide levels during wet (114 ng/l) and dry season (1 ng/l) which can be explained by seasonally altered run-off from agricultural surfaces. In this study, pesticides were found in the shallow aquifer and well water whereas they were absent in a deeper aquifer illustrating the vulnerability of shallow groundwater.

Pesticides are a heterogeneous group with varying degradation and sorption properties (Tuxen *et al.*, 2000). The fate of pesticides during subsurface passage depends on redox conditions, temperature, sorption processes as well as organic and water content in soil. Soils with moderate-to-high organic matter and clay content will adsorb pesticides onto soil particles.

In table 5, the observed reductions for several pesticides during bank filtration are displayed. The degradation potential for pesticides during bank filtration shows large variances and renders general predictions difficult. Levels in bank filtrate are further influenced by the extent of pesticide use, flow and run-off regimes.

The importance of sufficient retention times and necessity for microbial adaptation was shown in aerobic, aquifer material filled columns that were spiked with 25 µg/l of selected pesticides. Isoproturone and 4,6-Dinitro-*o*-cresol (DNOC) were significantly retarded by sorption while retardation for bentazone, MCPP, dichlorprop and 2,4-D was low. Only after a lag time of 16-33 days for MCPP, 2,4-D and dichlorprop and 80 days for DNOC, the substances were degraded (1.3-2.6 µg/l per day) (Tuxen *et al.*, 2000). Verstraeten *et al.* (2002) demonstrated for the herbicides triazine and acetamide that degradation by bank filtration (33%) and subsequent ozonation (41%) shifted the burden of contamination from parent compounds

to metabolites. It should be taken into consideration that metabolites may also be persistent and harmful (e.g. DDT metabolites). Data on metabolites and their sorption properties is scarce rendering reliable predictions on degradation patterns difficult (Bergström & Stenström, 1998; Gilliom, 2001).

Table 5: Degradation of pesticides during subsurface passage

Pesticide	Reduction	Conditions	Reference
2,4-D	86 - >97%		Schmidt, 2003
Bentazone	0 – 60%	20 to >360 d	Schmidt, 2003
Bromoxynil	78 – 99%		Schmidt, 2003
Dichlorprop-P (2,4-DP)	30 – 50%		Schmidt, 2003
Flufenacet	63%	suboxic BF, 6 d	Schmidt, 2003
Glyphosate	17 - >30%	anoxic BF, 30-300 d	Schmidt, 2003
Isoproturone	10 - >75%		Schmidt, 2003
MCPA	74%		Schmidt, 2003
Mecoprop-P	0 – 80%		Schmidt, 2003
Metazachlor	40 - >99%		Schmidt, 2003
S-Metolachlor	0 - >70%		Schmidt, 2003
Metalaxyl-M	>75%		Schmidt, 2003
Terbuthylazin	10 - >70%		Schmidt, 2003
p,p'-DDA (DDT metabolite)	no removal		Heberer <i>et al.</i> , 2004
o,p'-DDA (DDT metabolite)	no removal		Heberer <i>et al.</i> , 2004

The findings of pesticides in groundwater many years after they have been banned, demonstrate that some substances are very persistent and even if a compound is degradable, little is known about the persistence and toxicity of its degradation products. The unidirectional flow from surface water to aquifer which is induced during bank filtration puts the aquifer at risk for contamination. Therefore, it is highly recommended to regulate pesticide use, apply well-studied, readily degradable pesticides only and implement land management practices (subsurface drains, irrigation and conservation tillage) and well management (Barbash & Resek, 1996). Generally, an improvement of surface water quality is to be expected after bank filtration because many substances are either partially or fully removed during subsurface passage. Bank filtration is also suitable to level off shock loads.

Developed countries still account for three-quarters of all pesticides used worldwide; but the use of pesticides is on the rise in developing countries (Miller, 2004). Since the 1950's, the overall pesticide use has increased 50-fold and was about 2.3 million tonnes per annum in 2002 (Miller, 2004). China has

meanwhile emerged as the world's second largest producer and consumer of pesticides. Surveys carried out in Brazil, Central America and Nigeria revealed that mishandling and overuse have put humans at risk for direct pesticide poisoning. Although pesticide levels in water bodies are estimated to be high, there is often no monitoring (Schwarzenbach *et al.*, 2006). The TECHNEAU investigations screened for 61 pesticides in the Yamuna river in Delhi (India) but no pesticides were detected above detection limit in this urban environment (Sprenger *et al.*, 2009). Developing and newly industrialised countries could benefit from the experience of developed countries with irresponsible pesticide use. However, this would require a surveillance authority deployed to develop regulations of use, means to monitor for different pesticides in the environment and take action against the illegal use of pesticides by involving and educating landowners.

2.2.8.2 Chlorinated hydrocarbons

- Chlorinated hydrocarbons become a problem with increasing industrialisation and irresponsible use or disposal, thus, this group is deemed an emerging concern in newly-industrialised countries
- Most chlorinated hydrocarbons are hydrophobic showing tendencies for sorption or bioaccumulation
- Degradation is influenced by the number of chlorine substituents and redox conditions as well as by the presence of co-metabolites as primary substrate
- Several persistent substances in groundwater systems are known and degradation rates can be extremely slow
- Shock loads, originating e.g. from spills, can be mitigated

Halogenated hydrocarbons are a group of chemicals composed of carbon, hydrogen and at least one halogen atom (Cl, F, I or Br). The focus in this chapter is on chlorinated hydrocarbons among which are many water pollutants of concern. Most of the pesticides meanwhile banned in western countries due to their toxicity are organochlorines (e.g. DDT, lindane). The bulk of disinfection by-products are also chlorinated hydrocarbons (e.g. trihalomethanes) formed during water disinfection. Chlorinated hydrocarbons are often toxic and persistent in the environment tending to accumulate in the food chain due to their hydrophobicity.

Apart from the sources mentioned above, chlorinated hydrocarbons find application in the degreasing of metals, circuit boards, textiles as solvents, cleaners, paint removers. They are employed in pesticide production, metal and chemical manufacturing. Sources for groundwater pollution include the leakage from point sources (e.g. industrial spills, waste disposal) and diffuse pollution sources (precipitation, surface run-off). Toxic chlorinated hydrocarbons that are found in measurable quantities in groundwaters adjacent to industrial sites include: dichloromethane (DCM), trichloromethane (TCM), tetrachloromethane (CTC), 1,1,1-trichloroethane (TCA), trichloroethene (TCE), tetrachloroethene (PCE), 1,2-dichloroethane

(1,2-DCA), *cis* and *trans* 1,2-dichloroethene (cDCE and tDCE), vinylchloride (VC), 1,2-dichlorobenzene (1,2-DCB) and 1,4-dichlorobenzene (1,4-DCB).

While in German drinking water regulations, a threshold for tetrachloromethane of 3 µg/l (TrinkwV, 2001) and a sum parameter for dichloromethane, tetrachloroethane, 1,1,1-trichloroethane and trichloroethane of 10 µg/l have been set, the WHO (2004) has devised guideline values for single chlorinated hydrocarbons:

TCE and PCE are strong cytotoxins and suspected genotoxins that should not exceed 70 and 40 µg/l, respectively. An anaerobic degradation product of the former two substances is the *cis*-form of 1,2-dichloroethene which is more predominant in groundwater systems than the *trans*-form. For both isomers a guideline threshold value of 50 µg/l applies. In the chain of degradation, the isomeric cDCE may be further broken down into vinyl chloride, a proven carcinogen in animals and humans with a recommended guideline value of 3 µg/l. For two other substances that are proven carcinogens in animals, 1,2-DCA and CTC, a guideline value of 4 µg/l has been set for each. The liver toxins DCM and 1,1-dichloroethene (1,1-DCE) shall not exceed 20 and 30 µg/l respectively. The most prominent disinfection by-products are THMs which shall not exceed 200 µg/l and guideline values for dichlorobenzenes have been recommended to be 300 and 1000 µg/l for 1,2-DCB and 1,4-DCB respectively.

In the groundwater environment, the low to moderate soluble chlorinated hydrocarbons (~ 0.2 to 20 g/l), may be found in significant depth and plumes of dissolved hydrocarbons can extend several kilometres. Substances with a water solubility higher 1 g/l are less subject to sorption (Rivett *et al.*, 2006).

Biodegradation is influenced by the number of chlorine substituents. Chlorinated hydrocarbons with less substituents are predominantly biodegraded under oxic conditions whilst the higher substituted (e.g. TCE, PCE, DCE) are rather biodegraded in the absence of oxygen. Field data studies from Noble & Morgan (2002) found half-lives for DCE at groundwater temperatures (10°C) to be 39 days under aerobic and 4.060 days under anaerobic conditions illustrating that long retention times may be required under unfavourable conditions. Bradley & Chapelle (1998) observed for the breakdown of DCE via VC to CO₂ a two times higher degradation under oxic conditions. The efficiency decreased from conditions of Fe (III) reduction to SO₄²⁻ reduction to methanogenesis, however, degradation was still evidenced under anaerobic conditions.

For bank filtration, chlorinated benzenes were shown by Schwarzenbach *et al.* (1983) to be eliminated within the first metres of infiltration at a faster rate than 1,4-DCB. The latter was non-degradable under anaerobic conditions. They also found 1,1,1-TCA, TCE and PCE to be persistent under aerobic and anaerobic conditions concluding that BF is unsuitable as first treatment step. This is in line with findings by Kühn & Müller (1988) reporting less than 10% reduction for TCE and PCE during bank filtration at the river Rhine.

However, in the same study THM and 1,4-DCB were removed between 40 to 60% and 1,2-DCB even between 60 to 90%.

From hazardous waste sites in Germany (250 sites) and the USA (500 sites), it is known that TCE and PCE are among the three most prevalent groundwater contaminants in both countries out of 25 micropollutants selected (also PAH & BTEX). In the USA, the list is headed by DCM while TCE is the most predominant pollutant in German groundwaters (Kerndorff *et al.*, 1992).

Biodegradation is influenced substrate-specifically by redox conditions and the availability of co-metabolites. Further, time necessary for relevant degradation may be long. Anaerobic degradation processes include dehalorespiration using the halogen as electron acceptor, direct anaerobic oxidation and anaerobic co-metabolism. Aerobic degradation processes are direct aerobic oxidation and co-metabolism. Dehalorespiration and co-metabolism both require an alternative substrate to be present (Rivett *et al.*, 2006).

Efficient shock load mitigation for the chlorinated hydrocarbon 1,2-DCA by bank filtration has been observed by Kühn & Müller (2000) where a peak concentration of 35 µg/l in surface water was seen 3 weeks later in bank filtrate. In bank filtrate, 1,2-DCA residuals showed a plateau concentration of 1 µg/l for 2-3 weeks.

Due to the diversity of chlorinated hydrocarbons and the complexity of degradation processes, a general prediction for their removal during BF is difficult. Low soluble compounds tend to sorb and degradation depends on redox conditions as well as the availability of co-metabolites as primary substrates. The persistence or extremely slow degradation has been observed for several chlorinated hydrocarbons (e.g. TCE, PCE) and in some cases, the metabolite (e.g. vinylchloride) exhibits a higher toxicity than its parent compound. Bank filtration may mitigate shock loads but is overall less suited to remove the chlorinated hydrocarbons discussed due to their persistence, long retention times and strongly diverging redox requirements.

It seems likely that newly-industrialised countries are considerably affected by chlorinated hydrocarbons as earlier suggested for pesticides, however, monitoring is yet scarce. Post-treatment of bank filtrate by GAC filtration may thus be necessary.

2.2.8.3 Aromatic hydrocarbons

- Increasing risk for water contamination by aromatic hydrocarbons in newly-industrialised countries due to rapid industrial growth
- Monocyclic aromatic hydrocarbons are better soluble in water and better degradable than PAHs due to structure and hydrophobicity
- PAHs are rather hydrophobic and tend to sorb to sediments and particles, thus, accumulating in the aquifer
- Experience has shown a long persistence in groundwater systems

Aromatic hydrocarbons are compounds that are characterised by a cyclic C-H-ring structure. They are usually distinguished into monocyclic and polycyclic aromatic hydrocarbons. Both, monocyclic (i.e. single ring structures) and polycyclic (two rings and more) aromatic hydrocarbons are regarded hazardous to aquatic ecosystems and human health due to the high toxicity combined with their persistence and spreading in the environment. They are often petroleum-derived compounds from heating oil, diesel or kerosene. The fate of aromatic hydrocarbons in the subsurface has been mostly studied in the context of site contamination by point sources (industrial sites, service stations, spills).

Monocyclic aromatic hydrocarbons

The most common monocyclic aromatic compounds are benzene, toluene, ethylbenzene and xylene which are collectively termed BTEX group. BTEX find application as fuel additives and solvents in many industrial processes. Because of their volatility as well as their relative hydro- and lipophilic properties, these toxicants are mobile within the hydro-, geo- and atmosphere. BTEX can act neurotoxic, mutagenic, teratogenic and carcinogenic. Benzene is a proven carcinogen for which the WHO recommends in drinking water a guideline value of 10 µg/l. For the less toxic alkylated benzenes, the WHO guideline is 100 µg/l but they are already perceived by odour or taste at a few micrograms per litre (WHO, 2006). German drinking water regulations set a threshold of 1 µg/l for benzene (TrinkwV, 2001).

The BTEX group is moderately soluble in water and thus, mobile in water systems. They are also readily biodegraded in soil, especially when a BTEX adapted microbiota is present (Dou *et al.*, 2008, Da Silva & Alvarez, 2004). Degradation of BTEX was observed to occur rapidly under aerobic conditions and is continued at a slower rate under nitrate-, iron- and sulphate-reducing conditions (Gelman & Binstock, 2008; Alfreider & Vogt 2007; Botton & Parsons, 2006, Tiehm & Schulze, 2003). Mean half-lives for BTEX compiled by the Rivett *et al.* (2006) from Noble & Morgan (2002) were <220 days under aerobic conditions and <519 days under anaerobic conditions. Dou *et al.* (2008) reported that BTEX was degraded to non-detectable limits within 70 days by an adapted microbial consortia under anaerobic conditions when

concentration in soil were <100 mg/kg. Degradation was observed to be best in the order: toluene >ethylbenzene >m-xylene >o-xylene >benzene >p-xylene. Gelman & Binstock (2008) observed at a petroleum-contaminated aquifer near Tel Aviv, that at the source of contamination anaerobic conditions established and complete degradation of BTEX occurred within 100 m groundwater flow.

Degradation further depends on the presence of co-nutrients. Ethanol may sometimes be present along with BTEX in gasoline spills. It can hinder BTEX degradation due to the preferential degradation of ethanol and the depletion of nutrients and electron acceptors (Da Silva & Alvarez, 2002). As illustrated above, within the BTEX group, some substances are faster degraded than others, for instance, toluene is faster degraded than benzene (Da Silva *et al.*, 2004, Dou *et al.*, 2008). However, the addition of sodium acetate and/or ethanol has elsewhere been suggested to boost microbial activity and enhance a temporally delayed BTEX degradation (Oesterreicher-Cunha *et al.*, 2008; Dou *et al.*, 2008).

Although some studies have suggested the complete degradation of BTEX within 70 days or within 100 m is possible, petroleum-derived hydrocarbons leaching into groundwater systems should be prevented by all means. Groundwater protection from spills and industrial waste is best achieved by spatial separation and the establishment of groundwater protection zones. In case of surface water contamination (typically occurring in peaks), bank filtration systems have a certain capacity to mitigate shock loads and degrade the pollutants; however, degradation may take months and the concomitant changes in redox zonation are likely to impair the overall cleaning capacity of bank filtration.

Polycyclic aromatic hydrocarbons

Polycyclic aromatic hydrocarbons (PAH) consist of two or more aromatic rings. Generated as by-products from incomplete combustion processes from organic matter as well as during wood and metal treatment, they are ubiquitously found in the environment. Their toxicity, persistence and tendency for bioaccumulation render them a risk to wildlife and human health. Also the combined and additive effects have been reported to be a concern to aquatic organisms (Landrum *et al.*, 2003). Polycyclic aromatic hydrocarbons account for the most toxic fraction of tobacco smoke and are often found associated with other micropollutants such as chlorinated biphenyls (PCBs) and organochlorine compounds such as DDT (Maruya & Home, 1996).

Among the several hundred identified, 16 PAH are listed by the US Environmental Protection Agency as "priority pollutants". The group of polycyclic aromatic hydrocarbons is also classified by the EU water policy as "priority hazardous substances". The German Drinking Water Regulation has set a threshold of 0.01 µg/l for benzo(a)pyrene (WHO guideline: 0.7 µg/l) and a threshold of 0.1 µg/l for the sum of PAH. The latter is calculated from

the concentrations of benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(ghi)perylene and indeno(1,2,3-cd)pyrene.

Benzo(a)pyrene is the most studied PAH, a known carcinogen, that is commonly used as indicator for PAH. Carcinogenicity to humans has been evidenced by inhalation and dermal exposure, not the oral route. The main source of PAH (chiefly: fluoranthene) in drinking water are old coal-tar coatings of distribution pipes, however, no guideline value has been proposed for fluoranthene as concentrations are not considered to constitute a risk to human health (WHO, 2006).

In the subsurface environment, the degradability of PAH is influenced by their structure, redox conditions, the availability of co-nutrients and to a minor extent by temperature and pH. The ring structure affects water solubility and sorption. Water solubility decreases with increasing molecular weight almost logarithmically (Johnsen *et al.*, 2005) and higher ring numbers promote sorption. The two-ringed naphthalene is with 30 mg/L the most soluble PAH which is still several times lower than the monocyclic aromatic hydrocarbon benzene with 1.8 g/l (Wege, 2005).

PAH are less biodegradable than the BTEX group due to a more complex structure and their tendency to associate with solids and colloids. The association with particles may allow them to migrate deeper into the aquifer where sediment texture is coarse (Wege, 2005). Within the PAH group, the water soluble PAHs are metabolised faster due to the better bioavailability (Kästner *et al.*, 1993). The higher the organic carbon content found in aquifers, the more likely is the adsorption of PAHs. Brown & Maher (1992) examined sediment samples in the Georges River estuary in Australia and found that PAH concentrations in sediment were highest in areas with high silt, clay and organic matter content.

Wege (2005) has reviewed literature reporting the degradability of 2 to 4-ring PAHs under aerobic conditions while for PAHs composed of more than 4 rings, only for the 5-ring PAK benzo(a)pyrene microbial breakdown had been evidenced. Under reducing conditions (nitrate-, iron- and sulphate-reducing), only 2 to 3 ringed PAHs were observed to be degradable. Degradation of PAHs was seen to be more efficient under oxic condition while in the absence of oxygen considerable lower degradation rates are observed (Maher & Aislabie, 1992, McNally *et al.* 1998, Johnson *et al.*, 2005; Delaune *et al.*, 1981). Yuan & Chang (2007) compared reducing conditions in river sediments and found that PAH are better degraded under sulfate-reducing than under methanogenic than under nitrate-reducing conditions. The order in which four 3-ringed and one 4-ringed PAH (pyrene) were observed to be degraded best was: acenaphthene >fluorene >phenanthrene >anthracene >pyrene (Yuan & Chang, 2007).

The availability of nutrients (N, P) and substrates (other carbon sources) may considerably promote or inhibit the degradation of PAH. On the one hand, other available carbon sources may deplete available electron acceptors and

nutrients; on the other hand they may boost microbial activity. The addition of electron donors (acetate, lactate and pyruvate) was observed to enhance PAH degradation under anaerobic conditions and inhibit degradation under nitrate-reducing conditions (Yuan & Chang, 2007). The presence of naphthalene was shown to stimulate the degradation of phenanthrene and pyrene 5-fold and 2-fold respectively (McNally *et al.*, 1999).

Further, pH and temperature may influence degradation efficiency. Delaune *et al.* (1981) reported that degradation of benzo(a)pyrene in soil was considerably higher at pH 8 than at pH 5. In lab-scale experiments with aerobic river sediment, optimal conditions for phenanthrene degradation were at near neutral pH and 30°C. The significance of temperature may vary as was demonstrated by Eriksson *et al.*, (2003) reporting that low temperature inhibited PAH degradation under aerobic but not under nitrate-reducing conditions (Eriksson *et al.*, 2003).

Polycyclic aromatic carbons are not as biodegradable as BTEX and their tendency to sorb to particles and sediments renders them less bioavailable. Aerobic conditions are deemed most favourable for PAH degradation while it is slowed down under anaerobic conditions. These factors render general predictions on PAH degradation during bank filtration difficult and there is a lack of field studies in literature. Therefore, as for monocyclic aromatic hydrocarbons, it is recommended to rather avoid groundwater contamination by taking measures of source protection.

Aromatic hydrocarbons in developing and newly-industrialised countries

Aromatic hydrocarbons are typical by-products derived from industrial manufacturing and the use of fossil fuels. The spreading of these toxic micropollutants in the environment is thus likely to rise in countries where economic and industrial growth obtains priority over environmental and health considerations. Quickly growing economies such as the populous newly-industrialised countries China and India account already for one third of the global crude oil demand and further deterioration of water quality is likely to occur. In an industrialised part of China, PAH concentrations in 10 rivers were examined and found to range between 45.8 and 1.276 ng/l (mean: 174.1 ng/l) (Shi, 2003).

Bank filtration holds potential to remove micropollutants (sorption, degradation) and mitigate shock loads that are present in surface water. However, the time required for degradation can be several months to years (especially under anaerobic conditions) and complete degradation of the toxic substances is uncertain. The shift of redox conditions following pollution may impair the overall cleaning capacity. Therefore, it is more sensitive to invest into source water protection.

2.2.8.4 Endocrine disrupting chemicals

- Developing and newly-industrialised countries are affected by EDC particularly due to the use of organochlorine pesticides and rapid industrial growth
- Many EDCs are hydrophobic and removable by sorption
- > 90 % removal possible for Bisphenol A, estradioles, nonylphenols and octylphenols under oxic conditions, though a lag-time may be required

Endocrine disrupting chemicals (EDCs) are exogenous, either natural or synthetic, substances that mimic hormones and hence interfere with the endocrine system. Endocrine disruptors can be cleaners, pesticides, food additives, cosmetics, contraceptive drugs or even inorganics such as heavy metals. Although the risk posed to human health is little understood, concerns have been expressed regarding their cumulative and synergistic effects (e.g. infertility). In the aquatic ecosystem which serves as an early warning system for environmental toxins, the feminisation in male fish has been observed (CEH, 2002; Jobling & Tyler, 2006). Endocrine disrupting chemicals are omnipresent in industrial and domestic wastewater and often incompletely removed by sewage treatment. Thus, it is important to know for BF operation whether EDCs present in surface waters can be removed by subsurface passage.

Endocrine disrupting chemicals (EDCs) encompass a large group of chemicals. The important group of pesticides (many of which are endocrine disruptors) is discussed separately (Ch. 2.2.8.1 Pesticides). There are no WHO guideline values for endocrine disrupting chemicals in drinking water (except for pesticides). Non-pesticides that interfere with the endocrine system and are commonly found as pollutants in the environment are estradioles, bisphenol A (BPA), n-nonylphenoles (NPs) and octylphenoles (OPs).

Estradioles

Estradioles, estrones and estriols are sex hormones belonging to the group of human estrogens. The estradioles 17 β -estradiole (E2) and 17 α -ethinylestradiole (EE2) are prescribed as contraceptives. The endocrine effect of E2 and EE2 in male fish is with 1-10 ng/l and 0.1 ng/l respectively very low (Routledge *et al.*, 1998; Purdom *et al.*, 1998). Estradiols are hydrophobic and tend to sorb to soil sediments (Sangsupan *et al.*, 2006). Half-lives of estradiol were <0.5 d and 0.2 d in aerobic and anaerobic soil columns respectively (Ying *et al.*, 2008). Estradioles have been reported to be below the detection limit in bank filtrate after the first metres of infiltration under aerobic conditions (Zühlke *et al.*, 2004).

Bisphenol A

Bisphenol A (BPA) is a common industrial product (2.8 million tons produced in 2002) finding large application in the manufacturing of polycarbonate and epoxy resins. It was found to leach from plastic bottles and was evidenced to act as xenoestrogens in amphibians (Levy *et al.*, 2004). The effect on humans is disputed, however, it has been recently reported that BPA is transformed within the human body into a metabolite that does not have an estrogenic effect and is readily excreted via urine (BfR, 2007). There is inadequate evidence for the carcinogenic or mutagenic effect on humans. A study investigating the fate of BPA in seven European and US American rivers showed that following a lag phase of 2-4 d, the biodegradation half-lives were typically less than 2 days. Klecka *et al.* (2001) concluded that BPA is not persistent in the aquatic environment. At a bank filtration site near the river Rhine where concentrations in surface water average about 50 ng/l. BPA was usually not detectable in bank filtrate in a 3-year observation period (Sacher *et al.*, 2000).

Nonylphenols and octylphenols

Nonylphenols (NPs) and octylphenols (OPs) are degradation products of alkylphenol polyethoxylate surfactants. Both find application in industrial cleaning, paint production and emulsion polymerization. Nonylphenols and their ethoxylates are classified as "priority hazardous substances" by EU water policy with regard to their toxicity and persistence (WRRL, 2000). Octylphenols, which are only produced in small amounts in Germany (2000: 2.100 t), are currently under review for the classification as "priority hazardous substance". The concentration of 4-n-nonylphenols (4-n-NPs) was observed to have decreased in German surface waters due to the implementation of the European Directive 2003/53/EG that restricts the marketing and use of nonylphenols (Quednow & Puttmann, 2008). NP and OP concentrations in surface waters are commonly in the nanogram range.

The endocrine disrupting effects of NP and OP have been evidenced for marine and freshwater species (e.g. fish, daphnia), birds and mammals but not humans (CEH, 2002; Jobling & Tyler, 2006, White *et al.*, 1994; Bangsgaard *et al.*, 2006). Due to its low solubility, n-nonylphenol tends to bioaccumulate to a significant extent in aquatic species and 10 to 20 µg/l may exhibit estrogenic activity, however, this is 3 to 6 orders lower than for estradiols. One of the most potent EDCs, 4-tert-octylphenol (4-t-OP), has only a moderate potential potential for accumulation but may sorb to organic matter in soil, sediments and mud. The effect of OP resembles to 17β-estradiol, however, 1000-fold greater concentration are necessary (White *et al.*, 1994).

Abiotic degradation is found negligible for NPs, but because of their hydrophobicity, they strongly adsorb to soil sediments. Nonylphenols and octylphenols are subject to biological degradation. Yuan *et al.* (2004) observed that under aerobic conditions half-lives for NP were between 14 and 99 days in soil sediment adjacent to the river Erren (Taiwan). In Switzerland, high surface water concentrations ranging between 1.8 and 25 µg NP/l were seen

to be reduced to <1 µg/l after 2.5 m of subsurface passage (Schaffner, 1987; Ahel *et al.*, 1996).

In lab-scale experiments conducted by Ying *et al.* (2008) efficient degradation was observed for E2, EE2, BPA, 4-t-OP and 4-n-NP in aquifer materials under oxic conditions while under anoxic conditions, E2 was the only substance degraded. Half-lives were in oxic aquifer material between 0.2 and 4.1 days. The data compiled in table 7 suggests that an efficient removal is achievable during BF under aerobic conditions depending on the length of the oxic passage.

Table 7: Degradation of endocrine disruptors during subsurface passage

Substance	Reduction	Days (d) or distance (m)	Conditions	Reference
BPA	> 99 %	n.a.	BF, c ₀ = 50 ng/l	Sacher <i>et al.</i> , (2001)
	50 %	0.2 to 4.1 d	oxic aquifer material columns	Ying <i>et al.</i> (2008)
	> 99 %	n.a.	oxic (BF)	Schmidt <i>et al.</i> (2003)
	>95%	60 to 100 d	oxic	Schmidt, (2003)
	> 99 %	n.a.	anoxic	Sprenger <i>et al.</i> (2009)
E2 and EE2	> 99 %	first metres of BF	oxic	Zühlke (2004)
	50 %	26 d for E2, 0.2 to 4.1 d for EE2	oxic aquifer material columns	Ying <i>et al.</i> (2008)
NP	50 %	14 to 99 d	oxic	Yuan <i>et al.</i> (2004)
	70%	14 m	c ₀ = 1 µg/l oxic?	Schaffner (1987)
	93%	5-14 m	c ₀ = 2.7 µg/l suboxic	Ahel (1996)
	50 %	0.2 to 4.1 d	oxic aquifer material columns	Ying <i>et al.</i> (2008)
	> 95%	n.a.	oxic (BF)	Schmidt <i>et al.</i> (2003)
NP M	50 %	1) 69 to 116 d	1) oxic	1) Yuan <i>et al.</i> (2004)
	98-99%	1-14 d	suboxic BF	Ahel (1996)

Substance	Reduction	Days (d) or distance (m)	Conditions	Reference
OP	50 %	0.2 to 4.1 d	oxic	Ying <i>et al.</i> (2008)

BPA = bisphenol A, E2 = 17 β -estradiole, EE2 = 17 α - ethinylestradiole, NP = nonylphenol, OP = octylphenol, NPM = nonylphenol monoethoxylate

The endocrine disrupting chemicals reviewed share a hydrophobic character which limits their mobility in groundwater systems and promotes their sorption to soil sediment. The retained substances can then be degraded. It has been proposed that non-pesticides such as bisphenol A interfering with the endocrine system are not persistent in the environment and the studies compiled in table 7 indicate that they are degradable under oxic conditions. Degradation either already occurs in surface water or within the first 15 m of infiltration but a lag-time for microbial adaptation may be necessary. However, their persistence under anoxic/anaerobic conditions has been suggested (Ying *et al.*, 2008). Pesticides some of which are potent endocrine disruptors, were shown to exhibit a highly variable degradation behaviour (Ch. 2.2.8.1 Pesticides). Redox conditions and temperature were reported to influence degradation.

Concerns have been raised that developing and newly-industrialised countries are particularly exposed to endocrine disrupting chemicals due to excessive use of pesticides and rapid industrial growth. Several organochlorine pesticides which are banned in industrialised countries because of their toxic properties are still used in low-income countries (Ch. 2.2.8.1). Exponential industrial growth and in particular, the production of plastics contribute to the release of endocrine-disrupting chemicals into the environment. According to the Society of the Plastics Industry (1997), the sector of plastics industry has grown in the US at the rate of 6-12% per year in the 1990s while in developing countries, the annual growth rate was already 40% often without any precautions taken to protect the environment.

Although there is currently scarce evidence that endocrine disrupting chemicals can cause health problems to humans at the low levels found in drinking water, the cumulative and synergistic effects of endocrine disruptors remain a concern. Adverse effects have been observed in aquatic organisms which function as an early warning system for environmental toxins. Bank filtration is suitable to remove several endocrine disrupting chemicals by sorption and degradation under oxic conditions. However, some (especially organochlorine) pesticides can be persistent.

2.2.8.5 Pharmaceuticals

- Pharmaceuticals in drinking water are of minor importance in developing countries due to lacking or limited health care, sanitation and infrastructure
- Newly-industrialised countries will see a rise of pharmaceuticals in water sources, however, the implications on the environment and man are still uncertain
- degradability is compound-specific and redox-dependent, further by raw water quality, microflora present & previous exposure, redox conditions, temperature, retention time and compound characteristics (complexity, polarity)

Pharmaceuticals comprise a large and diverse group of chemicals, including human and veterinary medicines, which may enter the environment via excretion or disposal of unused medications. Many pharmaceuticals are not or only partially metabolised upon consumption and become excreted into sewage (Heberer, 2002). Pharmaceuticals commonly found in sewage include antibiotics (e.g. sulfamethoxazole), analgesics (e.g. phenazone), antiseptics (e.g. triclosan), anticonvulsants (e.g. carbamazepine), antidepressants (e.g. fluoxetine) and hormones (e.g. estrone).

With the exception of veterinary pharmaceuticals which find their way into water sources via the spreading of manure and surface run-off, pharmaceuticals are commonly released into the environment by point sources (e.g. STP effluent).

Pharmaceuticals can reach the consumer via surface water or contaminated, artificially recharged groundwater used for drinking water supply. Although the concentrations found in drinking water are far below medical doses, concerns have been expressed regarding their accumulation in the terrestrial and aquatic environment. Cumulative, combined and synergistic adverse effects on humans and aquatic organisms cannot be ruled out.

Steroid estrogens, which may act as endocrine disrupting chemicals, were demonstrated to contribute to feminisation in male fish (CEH, 2002; Jobling & Tyler, 2006). Furthermore, the extensive use of antibiotics has been suspected to trigger the emergence of antibiotic-resistant bacterial strains in the environment, however, acquisition of bacterial resistance is a process not yet fully understood (Alexy & Kümmerer, 2006).

There is no WHO recommendation and no threshold value in German Drinking Water Guidelines, however, health-oriented benchmark values have been proposed for carbamazepine (0.3 µg/l), diclofenac (0.3 µg/l) and X-ray contrast agents (1 µg/l) by the German Federal Environmental Protection Agency (Bode *et al.*, 2008; UBA, 2003).

During subsurface passage, pharmaceutical and metabolite concentrations may (i) decrease due to biodegradation and adsorption processes, (ii) increase when they become desorbed (or be generated during degradation) or (iii) be persistent under the site conditions given. The analgesic dimethylaminophenazone (DMAA) was demonstrated to be degraded by more than 90% into the likewise biodegradable metabolite formylaminoantipyrine (FAA) but also into 1-acetyl-1-methyl-2-dimethyl-oxamoyl-2-phenylhydrazide (AMDOPH), a very persistent compound (Zühlke, 2004).

It is frequently observed for pharmaceuticals & other micropollutants that degradation commences only after a certain period of time (lag-phase). This is ascribed to the adaptation of the microbial community. In column experiments, Preuß *et al.* (2002) could demonstrate that carbamazepine required 17 days lag-time whereas degradation started within 5 days for bezafibrate, diclofenac, clofibric acid, gemfibrozil and ibuprofen. The lag-time was shown to coincide with changes in the microbial population analysed by Polymerase Chain Reaction (PCR) and Denaturing Gradient Gel Electrophoresis (DGGE) analysis.

It has been suggested that hydrophobic, non-polar compounds are more likely to interact with the sediment and adsorb (Verstraeten *et al.*, 2002), while higher temperatures promote their degradation (Grünheid *et al.*, 2008). However, phenazone has been observed to be fully degraded in winter months where oxic conditions prevailed but not under anoxic conditions in summer months (Greskowiak *et al.*, 2006; Massmann *et al.* 2006), thereby illustrating the importance of redox conditions.

Pharmaceuticals that have repeatedly been reported to be **redox-dependent and degradable best under oxic conditions** are dimethylaminophenazone (DMAA), phenazone and phenazone-type analgesics (Zühlke, 2004, Massmann *et al.*, 2006; Heberer *et al.*, 2004), as well as the estrogenic steroids 17 β -estradiole, estrone and 17 α -ethinylestradiole (Zühlke, 2004).

Pharmaceutical substances that have been reported to be redox-dependent and **degradable best under anoxic/anaerobic conditions** are sulfamethoxazole (Jekel & Grünheid, 2007; Schmidt *et al.*, 2003) and amidotrizoic acid (Schmidt *et al.*, 2003; Schmidt, 2003).

A **redox-independent and readily degradable** pharmaceutical is the X-ray contrast agent iopromide (Jekel & Grünheid, 2007).

Substances that have repeatedly been reported to be **difficult to break down during bank filtration irrespective of the redox conditions** include the analgesic-metabolite AMDOPH (Zühlke, 2004; Heberer *et al.*, 2004) and the two anti-convulsants primidone (Heberer *et al.*, 2004) and carbamazepine (Heberer *et al.*, 2004, Schmidt *et al.*, 2003; Sacher *et al.*, 2000).

In table 8, substances are classified into groups for which low removal efficiency (0-40%), medium removal efficiency (40-90%) and high removal efficiency (>90%) that has been observed during bank filtration. The column “conditions” provides explanatory information for the respective study on redox conditions (oxic, suboxic, anoxic), retention time (d) and well depth where this information was available.

Apart from a substance’s degradability and redox sensitivity, the degradation of pharmaceuticals is influenced by raw water quality, microbial adaptation (lag-times required), temperature, sorption and retention time. Since the removal of pharmaceuticals and metabolites during bank filtration shows large variations, it is difficult to make general predictions for yet unstudied substances rendering further investigations necessary.

Table 8: Overview of substance degradability during subsurface passage

Pharmaceutical	Removal	Conditions	Reference
Low removal (0-40%)			
AMDOPH (A)	0%	oxic BF, 3-50 d	Schmidt, 2003
	0%-70%	anoxic BF 80-240 d	
	0%	shallow monitoring well	Heberer <i>et al.</i> (2004)
Amidotrizoic acid (X)	95%	oxic BF	Schmidt <i>et al.</i> (2003)
	65-95%	anoxic BF, 80-240 d	Schmidt, 2003
Carbamazepine (V)	0%	shallow monitoring well	Heberer <i>et al.</i> (2004)
	<10%	(sub)oxic: >365 d ($t_{1/2}$)	Stuyfzand <i>et al.</i> (2007)
	0%	oxic BF	Schmidt <i>et al.</i> (2003)
	0-40%	oxic BF 7-100 d	Schmidt (2003)
	0-40%	anoxic BF 20-120 d	
Primidone (V)	0%	shallow monitoring well	Heberer <i>et al.</i> (2004)
Medium removal (40-90%)			
Clofibric acid (M)	40-90%	oxic BF 20-65 d	Schmidt (2003)
	59-75%	n.a.	Heberer <i>et al.</i> (2004)
Iopamidol (X)	0-90%	(sub)oxic: 25-85 d ($t_{1/2}$)	Stuyfzand <i>et al.</i> (2007)

Pharmaceutical	Removal	Conditions	Reference
	52%	oxic BF	Schmidt <i>et al.</i> (2003)
Propyphenazone (A)	20-90%	anoxic BF 20-120 d	Schmidt (2003)
	52-69%	shallow monitoring well	Heberer <i>et al.</i> (2004)
Sulfamethoxazole (B)	0-70%	sub)oxic: > 365 d ($t_{1/2}$), anoxic: 25-55d ($t_{1/2}$)	Stuyfzand <i>et al.</i> (2007)
	78%	oxic BF	Schmidt <i>et al.</i> (2003)
	70-90%	anoxic BF	Schmidt (2003)
High removal (>90%)			
Bezafibrate (M)	> 99 %	oxic BF	Kühn & Müller, 2000
	> 99 %	oxic BF	Schmidt <i>et al.</i> (2003)
	75-99%	anoxic BF, 20-120 d	Schmidt (2003)
Diclofenac (A)	>94%	oxic	Kühn & Müller, 2000
	98%	oxic BF	Schmidt <i>et al.</i> (2003)
	80->95%	oxic BF 7-100 d	Schmidt (2003)
	30-99%	anoxic BF 20-120 d	
Ibuprofen (M)	100%	anoxic	Sprenger <i>et al.</i> , 2009
Iomeprol (X)	>90%	(sub)oxic: <0.5 - <6 ($t_{1/2}$)	Stuyfzand <i>et al.</i> (2007)
	> 99 %	oxic BF	Schmidt <i>et al.</i> (2003)
Iopromide (X)	>90%	(sub)oxic: <7 d ($t_{1/2}$), anoxic: 140 - >365 d ($t_{1/2}$)	Stuyfzand <i>et al.</i> (2007)
	> 99 %	oxic BF	Schmidt <i>et al.</i> (2003)
	82->99%	anoxic BF 80-240 d	Schmidt (2003)
Metoprolol (M)	97%	oxic BF	Schmidt <i>et al.</i> (2003)
Phenazone (A)	> 99 %	(sub)oxic: <2 d ($t_{1/2}$)	Stuyfzand <i>et al.</i> (2007)

A = Analgesics, B = Antibiotics, M = Miscellaneous, V = Anticonvulsants, X = X-ray contrast agent

In developing countries, pharmaceuticals are unlikely to become an issue since the use of pharmaceuticals and the operation of sewage treatment facilities as major point sources are both characteristic for industrialised countries and developed infrastructures. It is further expected that different types of medicinal products such as anti-tuberculosics (e.g. isoniazide, pyrazinamide) or anti-malaria drugs (e.g. chloroquine, mefloquine) are more likely to be present in developing countries than for example, blood-lipid regulating agent like clofibrilic acid.

In newly-industrialised countries, the consumption and discharge of pharmaceuticals is likely to increase and the drugs used will reflect the level of sanitation and development. Ibuprofen, for instance, is a drug commonly prescribed in India and was found in Indian surface waters but not in bank filtrate (Sprenger *et al.*, 2009). Since little is known on the adverse effect of pharmaceuticals in drinking water, they are at present not in the focus of concern in developing and newly-industrialised countries.

2.2.8.6 Disinfection by-products (DBPs)

- Given the high organic loads in source water, DBP will become an issue where safety chlorination is carried out (i.e. increasingly in newly-industrialised countries)
- BF is deemed efficient to remove DBP precursors and most DBPs
- DBP removal is compound and site-specific (retention time, redox conditions and organic matter)
- Anoxic conditions appear to degrade the bulk of DBPs best

Disinfection with strong oxidants (e.g. chlorination, ozonation) is common practice in drinking water treatment to inactivate pathogens and ensure microbial water safety. In the 1970's, drinking water chlorination was recognised to form harmful, potentially carcinogenic disinfection by-products (DBPs) with organic matter that is present in source water (Rook, 1974, Singer, 1994). Further, DBPs have been proposed but not evidenced to cause adverse reproductive outcomes e.g. low birth weight (Nieuwenhuijsen *et al.*, 2000). There is also inadequate evidence for the carcinogenicity of chlorinated drinking water in humans and animals (IARC, 1991). However, not all disinfection by-products have been identified and are understood (Richardson *et al.*, 2007). Iodoacetic acid is an emerging DBP that has only recently been recognised as one of the most cyto- and genotoxic by-products to mammalian cells (Cemeli *et al.*, 2006). Therefore, DBPs in drinking water constitute a potential risk requiring more investigation. The main DBPs identified are:

- trihalogenmethanes (THMs),
- halogenated acetic acids (HAAs),

- (halo)acetonitriles,
- chloral hydrates,
- cyanogen chlorides,
- chlorophenols
- and bromates (USEPA, 1999; WHO, 2002b).

Trihalogenmethanes account for 90% of the by-products produced with the major component being chloroform (>90%). The other three THM species are bromodichloromethane, dibromochloromethane and bromoform. German drinking water regulations set threshold values of <0.05 mg/L and <0.1 mg/L for THMs and bromate respectively (TrinkwV, 2001). International standards for THM vary between 0.025 and 0.25 mg/L (WHO, 2006). However, it is emphasised in all guidelines that the inactivation of pathogens has the utmost priority as the health risk from DBP is several orders of magnitude lower than the risk associated with inadequate disinfection (WHO, 2002b).

The formation of disinfection by-products depends on the disinfectant used (e.g. chlorine, chloramine, chlorine dioxide, ozone, iodine), the dosage, the presence of DBP precursors (organic matter), temperature and pH (Whitaker *et al.*, 2003; WHO, 2006). In the United States, chlorine is the most common disinfectant, followed by the weaker chloramine. Increasingly, ozonation is gaining popularity for its effectiveness against chlorine-resistant pathogens like *Cryptosporidium* oocysts. However, all disinfectants are oxidants and produce by-products, e.g. ozone reacts to the health-relevant bromate in the presence of bromide (Bonacquisti, 2006).

Since the removal of DBPs via activated carbon adsorption or air stripping is not efficient, the emphasis is commonly placed on precursor removal which is also reflected in the availability of literature and guidelines. The US Disinfectant/Disinfection Byproducts Rule (D/DBPR) stipulates the TOC concentration to be <2 mg/L prior to disinfection (USEPA, 2001). In this context, bank filtration has often been advocated to be a useful pretreatment tool for the removal of NOM (Weiss *et al.*, 2003; Weiss *et al.* 2004; Drewes & Summers, 2002; Partinoudi & Collins, 2007). Weiss *et al.* (2003) reported that at three BF sites precursors for THMs and HAAs were removed between 50 and 80% and other DBP precursors between 30 and 100%.

In comparison to precursor removal, the fate of the actual DBPs during bank filtration has received less attention, likely because disinfection is usually carried out as the final drinking water treatment step in the multi-barrier system. Disinfection by-products may be found in surface water due to point sources such as STP, especially where sewage receives disinfection before it is discharged. Studies conducted in South Australia and the US at eight ASR sites and lab-scale experiments showed that DBPs can be removed by aquifer storage (Pavelic *et al.*, 2004; Pavelic *et al.*, 2005). Removal of HAAs and brominated THM species was observed to occur rather quickly irrespective of redox conditions, whereas the removal of chlorinated THM species is considerably more efficient under anaerobic (sulphate-reducing) conditions

(Pyne, 2006; Pavelic *et al.*, 2004). THMs half lives were >1 to 65 days (bromoforme better degradable than chloroform) while HAA attenuation was reported within 1 day. THM attenuation rates were found to vary more than two orders of magnitude (t_{90} of < 3 to >400 days) (Pavelic *et al.*, 2004; Pavelic *et al.*, 2005). Haloacetonitriles (HANs) are primarily removed by hydrolysis whereas THMs and HAAs are primarily biodegraded and hydrolysis or sorption processes are of minor importance (Pavelic *et al.*, 2004).

DBP removal is thus compound- and site-specific with redox conditions in the subsurface being a major factor influencing degradation. The presence of TOC is likewise important for chlorine residual to dissipate so that microbial degradation can occur and redox conditions turn anoxic. In an aquifer with low carbon where conditions did not turn reducing, fully and slight degradation within the first two months was observed for HAAs and THMs respectively and then THM reduction levelled off (Pyne, 2006). Pyne (2006) proposed representative degradation times for ASR wells in the US to be 9 days and 9 weeks for HAAs and THMs respectively.

The above-mentioned ASR studies suggest for BF that complete DBP removal is possible when retention times and carbon content are sufficient. Retention times necessary are best deduced site-specifically for the removal of chloroform which is one the most prevalent and persistent DBPs. In contrast to the readily degraded HAAs, it has been shown for some DBPs such as THM that redox conditions significantly determine removal efficiency. With regard to the ineffective degradation of chlorinated THM species under oxic conditions, anoxic aquifers have been suggested to be most suitable for DBP reduction (Pavelic *et al.*, 2005).

Bank filtration is an ideal pre-treatment step that not only reduces pathogen load (Ch. 2.2.3 Pathogens) but also DBP precursors (organic matter) and actual DBPs if present in source water. For the developing and newly industrialised countries that abstract drinking water from microbially contaminated source water, disinfection is indispensable. Microbial safety is of utmost importance and has priority over health risks potentially associated with DBPs.

3 The potential of BF for developing and newly-industrialised countries

The filtration potential of BF has been recognised early and been common practice in Europe for more than 100 years to improve surface water quality for drinking water production. The purpose of this report is to assess whether BF may constitute a valuable technique either as a pre-treatment or main treatment step for drinking water production in developing and newly-industrialised countries.

Developing and newly-industrialised countries are often located in tropical, semi-arid and arid climate zones being subject to weather extremes such as monsoon, floods and droughts. In combination with scarce freshwater resources, on-going, explosive urbanisation and the rise of megacities, this constitutes a challenge to local water supply. By the year 2010, more than half of the world's population is expected to live in cities (IHP, 2006). Urban settlements compete with rural areas for water where livestock farming and intensified land use by agriculture is on the rise to meet the demands of a growing population.

This development deteriorates surface water quality and depletes freshwater resources. A groundwater boom in large regions of Southeast Asia has already triggered the decline in groundwater levels causing wells to run dry and energy costs to rise. In this context, BF may give relief by replenishing the stressed groundwater resources with surface water which in addition receives treatment during subsurface passage. BF has been stated to be a low-tech method, relatively easy to integrate with existing technology and to operate requiring little maintenance (Partinoudi & Collins, 2007).

The location of developing and newly-industrialised countries in warmer climate zones sets different basic conditions compared to Central Europe. As groundwater temperature follows the annual average of air temperature, it is expected for these countries to be 10° to 20°C higher than the German mean groundwater temperature of 10°C. This affects the concentration of dissolved oxygen (colder water dissolves more oxygen) and is likely to promote microbial activity. In combination with sufficient amounts of biodegradable DOC, biodegradation is expected to cause a shift to reducing redox conditions faster than what is observed in Central Europe. In the absence of oxygen, many degradation processes are retarded and some contaminants can be remobilised from the sediment.

Weather extremes such as droughts and floods render water sources more vulnerable to contamination. During periods of low precipitation, there may not be enough water to dilute contaminants and during wet seasons, rivers carry high loads of mobilised, suspended matter. Rivers in the southern hemisphere generally carry large quantities of suspended matter. Equatorial riverine systems are estimated to carry about 60% of the world's total suspended load originating from the Indo-Pacific archipelago where high

relief and rainfall result in high sediment yields (Meybeck, 1988; Ramesh *et al.* 1995). For the river export of total suspended solids to coastal seas, Asia (50%), South America (20%) and Africa (12%) are the three main contributors. Bank filtration is efficient to remove suspended solids, however, enhanced clogging of the infiltration zone is likely to be observed and may render BF not sustainable.

Heavy rainfall may wash contaminants (e.g. pathogens, fertiliser, pesticides) into the surface water. Increased flow velocities in the subsurface are unfavourable for sorption and degradation processes, especially in coarse-grained sediments. Pathogens in drinking water are the major concern for human health. In many developing and even newly-industrialised countries, surface waters are used concomitantly as drinking water source and sewers, receiving insufficient or no water treatment. Lack of sanitation and access to safe water causes 2.2 million deaths/a, mostly affecting children in the developing world. Warm climate and eutrophic water bodies promote proliferation of certain pathogens and in combination with poor hygiene also give rise to species no longer seen in industrialised countries (e.g. parasitic worms). Bank filtration holds good potential for pathogen removal (sorption and inactivation) but BF schemes require thorough design in terms of long travel paths, retention time (50 to 100 days) and soil texture (sand aquifers) in order to comply with the strict guidelines that stipulate several log-removal for microbial contaminants. Nonetheless, additional safety chlorination is still recommended.

During infiltration, weathering processes between the aquifer material and the water phase alter the water chemistry. In the subsurface, sorption, precipitation/dissolution and ion exchange processes occur which depend on pH, salinity, ionic strength and redox conditions. The pH in groundwater system is usually near neutral pH but may slightly increase due to weathering in calciferous aquifers or decrease in pyritic aquifers under sulphide-oxidising conditions. Salinity is an important parameter since too high salt concentrations (noticeable taste: 100 mg Cl/l, non-potable: >400 mg Cl/l) render groundwater unsuitable for consumption. Especially in coastal areas, brackish aquifers may be found and dilution with less saline surface water is possibly the only low-tech process to reduce high concentrations.

Some developing and newly-industrialised countries such as India, China and Bangladesh are plagued with trace contaminants of geogenic origin (mainly As and F). This situation is further aggravated by malnutrition and lack of financial means to ease the problem (Ayoob & Gupta, 2006). In 70 countries, 137 million are at risk for arsenicosis and 200 million people in 25 countries are affected by fluorosis. But also the contamination with heavy metals of anthropogenic origin such as lead is seen as a significant problem in developing and newly-industrialised countries because of rapid industrial growth and lack of emission control. The removal potential of bank filtration for heavy metals ranges from 0 to 100% depending on redox conditions, pH as well as on the presence of suitable sorbents and counterions. Anoxic conditions (as expected to prevail in BF systems in developing and newly-

industrialised countries) are rather unfavourable for the removal of heavy metals due to the dissolution of sorbents, e.g. Fe (hydroxy-)oxides. At an anoxic BF field site in India, the TECHNEAU investigations found indeed elevated arsenic levels exceeding German drinking water standards in abstracted well water (Pekdeger *et al.*, 2008). The geochemical properties of an aquifer and the impact of water abstraction have to be determined site-specifically to ensure bank filtrate quality. In many cases, as in Central Europe, post-treatment may be necessary.

The expected prevalence of anoxic groundwater conditions is not a result of the warmer temperature alone. It is also influenced by the organic load carried in surface water. Where wastewater receives no treatment but is directly discharged into surface waters, the organic pollution is likely to be high and provides a carbon source to degrading, oxygen-consuming microorganisms. Thus, even in surface waters, as reported for the Yamuna river in India (Sprenger *et al.*, 2009), sulphate-reducing conditions can be found. Between 24 and 50% of the DOC were reported to be biodegradable by bank filtration, however, under anoxic/anaerobic conditions long retention times up to 3 months may be necessary. Another nutrient, nitrogen, may be present in the form of ammonia in faeces-contaminated waters or as nitrate that has been washed-off from agricultural surfaces. Under aerobic conditions, ammonia is microbially oxidised to nitrate (nitrification) while under anoxic conditions, nitrate is microbially reduced to gaseous N₂ (denitrification). The TECHNEAU investigations in India demonstrated that source water quality may become a major impairment to BF operation. High levels of ammonia, a typical indicator for faecal contamination, rendered BF alone unsuitable for drinking water production at a site in Delhi and would render additional treatment for ammonia removal necessary (Pekdeger *et al.*, 2008). Nutrients are usually not harmful at concentrations found in drinking water (the exceptions being nitrite/nitrate). Phosphate which is unstable in the environment and not a critical parameter to bank filtration, only becomes an issue when it is excessively present in surface waters. As limiting factor for growth, the presence of phosphate stimulates algal blooms resulting in growth, die-off and subsequent bacterial decomposition under oxygen depletion.

Some algal blooms (e.g. cyanobacterial blooms) release toxins harmful to humans. Bank filtration has been demonstrated to efficiently remove intracellular and extracellular microcystins which are the best studied algal toxins. The bulk of literature has been published in Europe, the U.S. and Australia, but studies from Asia, Africa and South America have confirmed that harmful algal blooms are a global issue. Factors promoting HABs are eutrophic water bodies and warm temperature, therefore, developing and newly-industrialised countries are considered particularly at risk.

The downside of industrialisation is the concomitant pollution of the environment. Organic micropollutants of anthropogenic origin are nowadays ubiquitously found in the environment of which many show adverse effects on humans, animals and aquatic ecosystems. Rapid industrial growth, lack of

emission controls and indiscriminate waste disposal have led to the distribution of organic micropollutants such as aromatic and chlorinated hydrocarbons in newly-industrialised countries. China and India account already for one third of the global crude oil demand. Studies from an industrial area in China reported concentrations of aromatic hydrocarbons (typical by-products from fossil fuels) in 10 rivers to range between 45.8 and 1,276 ng/l (Shi, 2003). Bank filtration holds potential to remove aromatic hydrocarbons (BTEX and PAHs) by sorption and degradation. It may also mitigate shock loads (e.g. spills) from surface waters. However, the time required for degradation may take months to years. Again the presumed predominance of anoxic/anaerobic conditions in developing and newly-industrialised countries is unfavourable for degradation since several hydrocarbons are very persistent under anaerobic conditions.

Some pesticides, especially the organochlorine pesticides such as DDT and lindane, are very persistent and tend to accumulate in the food chain. Many of the organochlorine pesticides exhibit endocrine disrupting effects and are considered carcinogenic. Developed countries still account for three-quarters of all pesticides used worldwide but the use of pesticides in developing countries is on the rise (Miller, 2004). China has meanwhile emerged as the world's second largest producer and consumer of pesticides. Surveys carried out in Brazil, Central America and Nigeria revealed that mishandling and overuse is putting humans at risk for direct pesticide poisoning. The pesticide levels in water bodies of developing and newly-industrialised countries is assumed to be high, though monitoring is lacking (Schwarzenbach *et al.*, 2006). The TECHNEAU investigations screened for 61 pesticides in the Yamuna river in Delhi but could not detect any pesticides above detection limit in this urban environment (Sprenger *et al.*, 2009). The removal of pesticides during subsurface passage is influenced by sorption (e.g. to clay material) and redox-dependent degradation. Bank filtration can improve water quality by complete or partial degradation as well as shock load mitigation from surface water but post-treatment such as GAC filtration may still be necessary.

In the form of organochlorine pesticides, chlorinated hydrocarbons are often toxic and persistent micropollutants that tend to sorb or bioaccumulate. They seem likely to be a problem wherever industrialisation is on the rise, however, the monitoring in newly-industrialised countries is yet scarce. Tetrachloroethane, dichloromethane, trichloroethene and cis-1,2-dichloroethene were the most common micropollutants found in German and U.S. groundwaters in proximity to industrial sites suggesting poor degradability. Degradability is influenced by the number of chlorine substituents, redox conditions and the presence of co-metabolites as primary substrates. Bank filtrations can mitigate shock loads but is less suited for the removal of chlorinated hydrocarbons due to long retention times necessary.

In developing and newly industrialised countries, the issues of endocrine disruptors and pesticides are closely linked. Organochlorine pesticides are potent endocrine disrupting chemicals, which are banned in industrialised

countries because of their toxic properties but they still find application in low-income countries. The exponential industrial growth and the production of plastics in particular, further contribute to the release of endocrine-disrupting chemicals into the environment. The plastics industry has grown in the U.S. at the rate of 6-12% per year in the 1990s while in developing countries, the annual growth rate was already 40%. Precautions to protect the environment are still uncommon. Several industrial by-products and pharmaceuticals of endocrine-disrupting potential (Bisphenol A, nonylphenols, estradiols) were observed to be removed well by BF. Due to their hydrophobic character, they tend to sorb and are often fully degraded under oxic conditions.

Disinfection of pre-treated water is generally recommended for developing, newly-industrialised and industrialised countries alike to ensure safe drinking water. It is known since the 1970's that the disinfection with oxidants generates harmful disinfection by-products when reacting with organic matter. Bank filtration is an ideal pre-treatment by considerably reducing pathogen loads (the aim of disinfection), by removing organic matter (DBP precursor material) and by removing disinfection by-products if present in source water.

Pharmaceuticals are not seen as critical water quality parameter in developing countries, since the use of pharmaceuticals and the operation of sewage treatment facilities as major point sources are both characteristic for industrialised countries and developed infrastructures. In newly-industrialised countries, the consumption and discharge of pharmaceuticals is likely to increase and the type of drugs used reflects the level of sanitation and development. The TECHNEAU investigations of the river Yamuna in India detected a number of stimulant residues (e.g. caffeine, cannabidiol) and ibuprofen. The latter is a common prescription drug in the area and was fully removed after subsurface passage (Sprenger *et al.*, 2009). Overall, little is yet known on the cumulative and synergistic adverse effect of pharmaceuticals on humans.

While pharmaceuticals are likely insignificant in developing countries, they are in the focus of concern in developed countries as emerging pollutants and not yet in the focus of interest of newly-industrialised countries. This illustrates the different emphasis placed on water contaminants based on the level of industrialisation.

In table 9, the parameters impairing water quality are listed and categorised into their relevance for developing and newly-industrialised countries (low, moderate, high). The potential of bank filtration to remove substances (poor, moderate, high) and possible quality limitations for bank filtrate are also given.

Table 9: Relevance of contaminants, BF removal potential and limitations

Parameter	Relevance for		BF removal	possible quality limitation by
	developing countries	newly industrialised countries		
Suspended solids	High	High	good	clogging
Pathogens	High	High	good	short travel times + coarse texture
Algal Toxins	High	High	good	coarse texture
Nutrients (C,N,P)	High	High	good to moderate	anoxic or anaerobic passage only
Anions & Cations	Low	Low	poor	salinity, missing oxic passage
Heavy metals (geogenic)	High	High	site and substance specific	
Heavy metals (anthropogenic)	Low to moderate	High	site-specific	missing oxic passage
Pesticides	Low to moderate	High	site and substance specific	
Chlorinated hydrocarbons	Low	High	moderate to poor	missing oxic passage
Aromatic hydrocarbons	Low	High	moderate	long attenuation especially anoxic cond.
Endocrine disrupting chem. (exc. pesticides)	Low	High	good to moderate	missing oxic passage
Pharmaceuticals	Low	Low to moderate	site and substance specific	

Parameter	Relevance for		BF removal	possible quality limitation by
	developing countries	newly industrialised countries		
Disinfection by-products	Low	Moderate to high	good	missing anoxic (!) passage

Bank filtration is a useful technique as pre-treatment or even as the main treatment step for drinking water. Pathogens, toxic algae and suspended solids which are deemed to be of high relevance to developing and newly-industrialised countries can be removed efficiently by BF. However, the overall cleaning capacity for organic and inorganic trace contaminants is often strongly redox-dependent and oxic conditions are favourable for contaminant removal by degradation or sorption to Fe and Al (hydroxyl-) oxides.

It is assumed that groundwater systems in developing and newly-industrialised countries tend to anoxic or even anaerobic conditions because of the organic pollution of source water (lack of wastewater treatment) and higher mean temperatures. Both are factors promoting microbial growth and may lead to oxygen depletion, thereby lowering the removal efficiency of BF systems. The TECHNEAU investigations in Delhi (India) found that surface water was sulphidic and ammonia levels in groundwater constituted a major impairment for BF operation. Further, the geogenic burden at a site (e.g. amounts of geogenic arsenic) requires thorough investigation prior to BF implementation.

The storage of stormwater in the subsurface is particularly useful in areas with strongly varying precipitation and run-off regimes and a suitable approach to manage freshwater availability. Although laws for source water protection can be enforced and the compliance controlled, education on the risks from unsafe water and the benefits of water treatment is just as important. The key to safe drinking water is source protection which is best achieved by gaining the support of the communities concerned.

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5 Appendix

Table 10: Removal of pathogens and indicators during subsurface passage

Pathogen or indicator	Travel time (d) or distance (m) to bank	Site	Removal efficiency (measured or estimated)	Reference
BACTERIA				
<i>Bacteria</i> spp.	2 m	“Bankside filtration”	3- \log_{10}	WHO, (2002a)
<i>Bacteria</i> spp.	4 m	“Bankside filtration”	4- \log_{10}	WHO, (2002a)
Total coliforms	11-19 d (84 m)	BF (Lake Naintal)	5- \log_{10}	Dash <i>et al.</i> , (2008)
Total coliforms	35 m	BF (Missouri River)	5.5 to 6.1- \log_{10}	Weiss <i>et al.</i> (2005)
Total coliforms	15 d (30 m) 63 d (25 m)	2 BF sites (River Meuse and River Rhine)	>5- \log_{10}	Schijven <i>et al.</i> (2002)
Faecal coliforms	11-19 d (84 m)	BF (Lake Naintal)	4- \log_{10}	Dash <i>et al.</i> , (2008)
Thermotolerant (faecal) coliforms	<15m	BF River Meuse, sandy gravel aquifer	4- \log_{10}	Medema <i>et al.</i> (2000)
Faecal streptococci	15 d (30 m)	BF River Rhine	>3.2- \log_{10}	Schijven <i>et al.</i> (2002)
Faecal streptococci	63 d (25 m)	BF River Meuse	>3.5- \log_{10}	Schijven <i>et al.</i> (2002)
<i>Bacillus</i> sp. (aerobic sporeformer)	27-177 m	3 BF sites (Ohio, Wabash & Missouri River)	0.8- \log_{10} to >3.1- \log_{10}	Weiss <i>et al.</i> (2005)
<i>Clostridium</i> sp. (anaerobic sporeformer)	27-177 m	3 BF sites (Ohio, Wabash & Missouri River)	0.4- \log_{10} to >4.9- \log_{10}	Weiss <i>et al.</i> (2005)

Pathogen or indicator	Travel time (d) or distance (m) to bank	Site	Removal efficiency (measured or estimated)	Reference
Spores of sulphite-reducing clostridia (SSRC)	13 m 18 d (25 m) 43 d (150 m)	BF River Meuse, sandy gravel aquifer	3.3- \log_{10} 3.9- \log_{10} 5.0- \log_{10}	Medema <i>et al.</i> (2000)
SSRC	63 d (25 m)	BF River Rhine	3.1- \log_{10}	Schijven <i>et al.</i> (2002)
SSRC	15 d (30 m)	BF River Meuse	3.6- \log_{10}	Schijven <i>et al.</i> (2002)
VIRUSES				
viruses	2 m	bankside filtration	3- \log_{10}	WHO, (2002a)
viruses	4 m	bankside filtration	4- \log_{10}	WHO, (2002a)
bacteriophage (male-specific)	13 m 18 d (25 m)	BF River Meuse, sandy gravel aquifer	3.9- \log_{10} 6.0- \log_{10}	Medema <i>et al.</i> (2000)
bacteriophage (male-specific)	27-177 m	3 BF sites (Ohio, Wabash & Missouri River)	2.1- \log_{10} to >2.6- \log_{10}	Weiss <i>et al.</i> (2005)
bacteriophage (male-specific)	15 d (30 m)	BF River Rhine	6.2- \log_{10}	Schijven <i>et al.</i> (2002)
bacteriophage (somatic)	13 m 18 d (25 m) 43 d (150 m)	BF River Meuse, sandy gravel aquifer	3.8- \log_{10} 5.1- \log_{10} 7.8- \log_{10}	Medema <i>et al.</i> (2000)
bacteriophage (somatic)	27-177 m	3 BF sites (Ohio, Wabash & Missouri River)	4.0- \log_{10} to >4.4- \log_{10}	Weiss <i>et al.</i> (2005)
bacteriophage (somatic)	1 m 4 m	BF (Yamuna River)	3.3- \log_{10} 4.6- \log_{10}	Sprenger <i>et al.</i> , 2009
bacteriophages MS2 & PRD1 (male-specific)	3- \log_{10} (after 2.4 m), 5- \log_{10} (after further 27 m)	dune infiltration	8- \log_{10}	Schijven <i>et al.</i> (1999)

Pathogen or indicator	Travel time (d) or distance (m) to bank	Site	Removal efficiency (measured or estimated)	Reference
bacteriophage PRD1 (male-specific)	<1 m	low organic matter, iron oxide-coated quartz sand and gravel aquifer	0.24-log ₁₀	Pieper <i>et al.</i> (1997)
bacteriophage PRD1 (male-specific)	<1 m	high organic matter iron oxide-coated quartz sand and gravel aquifer	0.77-log ₁₀	Pieper <i>et al.</i> (1997)
adenovirus	50 m	BF (Yamuna river)	>4- log ₁₀	Sprenger <i>et al.</i> (2009)
norovirus	50 m	BF (Yamuna river)	>4- log ₁₀	Sprenger <i>et al.</i> (2009)
reoviruses	13 m	BF Meuse River, sandy gravel aquifer	3.7-log ₁₀	Medema <i>et al.</i> (2000)
PROTOZOA				
protozoa		bankside filtration	4-log ₁₀	WHO, (2002a)
<i>Giardia</i> cysts		BF City of Kearney	2-log ₁₀	Schijven <i>et al.</i> , (2002)
<i>Giardia</i> cysts		BF Sonoma County	2.5-log ₁₀	Schijven <i>et al.</i> , (2002)
<i>Giardia</i> cysts	27-177 m	3 BF sites (Ohio, Wabash & Missouri River)	¹⁾ 1.3-log ₁₀ to >1.9-log ₁₀	Weiss <i>et al.</i> (2005)

Pathogen or indicator	Travel time (d) or distance (m) to bank	Site	Removal efficiency (measured or estimated)	Reference
<i>Cryptosporidium</i> oocysts	7.6 m to 15.2 m	Log-removal credited for BF in unconsolidated sand aquifer (10% fines)	0.5-log ₁₀ to 1.0-log ₁₀	USEPA, (2003)
<i>Cryptosporidium</i> oocysts	27-177 m	3 BF sites (Ohio, Wabash & Missouri River)	¹⁾ 0.9-log ₁₀ to >1.5-log ₁₀	Weiss <i>et al.</i> (2005)

¹⁾ no accurate determination possible (low and variable concentrations in river and well water)