



Part of D11.2:

Comparison of quantitative and qualitative data during MAR with aquifer baseline data – generic approach and site application in Berlin-Tegel



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Title: Comparison of quantitative and qualitative data during MAR with aquifer baseline data – generic approach and site application

Executive summary: This report assesses the impact of MAR on ambient groundwater, from the hydraulic and water quality perspective. Impact zones of MAR structures were divided into a) hydraulic impact zones and b) attenuation zones. Different transport processes of compounds during e.g. pond infiltration are schematically shown and explained below. Within this report, water quality data from one MAR site in Berlin-Tegel are compared to natural and anthropogenically influenced background values in the aquifer. Common approaches to determine background values in groundwater are introduced and described. At the MAR site in Berlin-Tegel, water quality parameters were observed in the infiltration pond (source water), in observation wells between the ponds and the production wells (impacted groundwater) and beyond the recovery wells (ambient groundwater). After hydraulic characterisation of the MAR site, observed concentrations of major ions, physico-chemical parameters, inorganic trace compounds, nutrients and organic trace compounds were compared with natural and anthropogenic background values (if any) by statistical plots.

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1 Comparison of quantitative and qualitative data during MAR with aquifer baseline data – generic approach and site application at Berlin-Tegel

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Managed aquifer recharge (MAR) is stipulated by the European Groundwater Directive (GWD) to be a supplementary measure to achieve 'good status' for 'all' water bodies by 2015 (EC, 2006). A 'good status' means both good quantitative status and good qualitative status. Good quantitative status is stipulated to be achieved if natural groundwater recharge exceeds groundwater abstraction. A good qualitative status is stipulated to be achieved when, among other criteria, if certain measured values for pollutants and indicators are in compliance with the threshold values. These threshold values are currently in discussion and to fulfill the objective of 'good status' in groundwater it is necessary to know the natural background values in groundwater, taking into account the geochemistry of the aquifer. Natural background values in groundwater can be defined as the regional (and depth dependent) background of a certain parameter, which would be present without any anthropogenic impact. In Germany, and especially in densely populated areas like Berlin, groundwater without any anthropogenic impact virtually does not exist. Therefore, it is important to differentiate between the natural and human impacted groundwater component.

In this section previously available methods to distinguish between anthropogenic and natural background level in groundwater are introduced. These background values, for selected inorganic and organic substances, from various studies are used and compared to measured values on site level in Berlin. Within this context, emerging pollutants are of special concern, since some have shown to be poorly degradable or may only be removed under specific redox conditions. The general approach followed in this report is described in Figure 1.





Figure 1-1: Description of approach to assess the impact of MAR on ambient groundwater.

1.1 General considerations on MAR impacts

The infiltration of water into an aquifer results in increased hydraulic pressure at the recharge zone. Depending on source water quality, travel time of infiltrated or injected water to the abstraction well, design of the MAR field site, and the purification capacity of the aquifer breakthrough of contaminants might be possible.

Impact zones of MAR structures can be divided into a) hydraulic impact zone and b) attenuation zone (Figure 2). Different transport processes of compounds during e.g. pond infiltration are exemplary shown in Figure 2.





Figure 1-2: Sketch of hydraulic and attenuation zonation during managed aquifer recharge.

The hydraulic impact zone is characterized by measurable hydraulic changes derived from the MAR system. The spatial extent and shape of the hydraulic impact zone mainly depends on:

• spatial distribution of hydraulic properties in the aquifer

• ambient hydraulic gradient in the aquifer (simplified to horizontal background groundwater level in Figure 2)

• pumping rates and interferences by pumping from other wells

The impact zonation is elongated in the direction of the ambient groundwater flow, but the spatial extent and shape of the hydraulic impact zone might differ substantially from site to site. In fractured or karstic aquifers the hydraulic impact zonation is more complicated and not transferable from Figure 2. The hydraulic impact zone is usually many times larger than the water-quality impact zone, especially for



confined aquifers.

The attenuation zone is the area surrounding the recharge zone where changes of the infiltrated water quality takes place due to natural processes in the aquifer. Depending on the compound and the geochemistry of the aquifer these processes include e.g. straining, degradation, sorption, dissolution/precipitation, inactivation (or die-off), decay and mixing. These natural attenuation processes may vary in time and space within the aquifer, particularly along the flow path from the area of recharge to the recovery well. Most attenuation processes in the subsurface occur at or close to the recharge zone. Part of the attenuation zone is the mixing, where ambient groundwater and the recharged source water mixes. Tracers are commonly used to distinguish between attenuation due to mixing and attenuation due to other reactions. A suitable tracer, or a set of tracers (e.g. chloride, $\delta 180$, δD), occurs in different concentrations in the ambient and the source water and allows to calculate mixing proportions and, in case of time variant tracer concentration also travel times.

While many contaminants get attenuated during subsurface passage to background level or below detection limit, some persistent compounds may get transported to the ambient groundwater or are introduced by the ambient groundwater (Figure 2). Sustainable removal is achieved when the recovered water meets the end-use requirements (e.g. drinking or irrigation water) in the recovery well(s) and the ambient groundwater meets the background levels of the aquifer. Ineffective removal is found when the recovered water exceeds end-use requirements and ambient background concentrations are not met. Apart from ineffective removal of compounds introduced by the MAR activity, another possible release mechanism of contaminants is secondary mobilization from the ambient groundwater or aquifer matrix. An example of contaminant mobilization by MAR activity through changes in the redox environment resulted from the MAR activity is given by Arthur et al. (2003). During Aquifer Storage and Recovery (ASR) testing in Florida (USA) oxygen-rich source water was injected into a confined limestone aquifer. Both source water and ambient groundwater had As concentrations < 10 μ g/l, but the concentrations in the recovered water were up to 112 μ g/l. Arsenic release was explained by oxidation of arsenic bearing pyrite present in trace concentration of the aquifer (Arthur et al., 2003).

Hydraulic and water quality monitoring is essential to assess the impact of MAR. At least one monitoring well is required to evaluate the impacts on ambient groundwater. This monitoring well should be situated down gradient of the MAR structure beyond the attenuation and hydraulic impact zone. But because of heterogeneities in porous aquifers it is recommended to use more than one monitoring well. In complex flow regimes, such as fractured or karstic aquifers, more monitoring wells are obligatory.

1.2 Assessing the effects of MAR on ambient groundwater resources in Berlin Tegel

1.2.1 Site description and characterisation

The site is located in the northwest of Berlin, where 3 infiltration ponds in the catchment area of Tegel Water Works are surrounded by about 40 production wells (Figure 3). The site is operated by the local water supplier (Berliner Wasserbetriebe). Aquifer recharge started in the late 1950's and from the 1960's three infiltration basins have been continuously used for infiltration (Greskowiak et al., 2006; Möller et al., 2011). Surface water from the nearby Tegel Lake is used as source water, pre-treated during summer by





filtering through a micro strainer (pore size diameter of 28 μ m) to prevent clogging by algae.

Figure 1-3: Overview of infiltration basins (Becken 1-3) and production wells (Brunnen) at the MAR site in Berlin Tegel with observation wells (Grundwasserbeobachtungsrohre).

The source water is influenced by treated wastewater from a wastewater treatment plant (WWTP) in the north of Berlin. The treatment process at the WWTP involves mechanical and biological treatment and additional chemical phosphate removal, nitrification and denitrification (Massmann et al., 2006). The share of treated wastewater in the infiltration pond is between 17-35 % (mean values from 1993-1998; Ziegler (2001)). The seven main components of the MAR site in Berlin Tegel are summarized in Table 1.



Recharge technique	MAR type
1. Enhanced infiltration	Surface water (lake Tegel) with 17-35 % of treated effluent
2. Pre- treatment	Microstrainer
3. Recharge	3 infiltration basins, approx. 9 Mm3/a
4. Sub-surface	Fluvio-glacial sediments, \geq 50 d residence time in the subsurface, oxic to Fe/Mn reducing conditions
5. Recovery	Fluvio-glacial sediments, \ge 50 d residence time in the subsurface, oxic to Fe/Mn reducing conditions
6. Post- treatment	aeration, slow sand filtration
7. End-use	Drinking water

Table 1-1: Brief summary of the seven components of the MAR system in Berlin Tegel

Impacted water quality is derived from samples taken from the monitoring wells situated inside the production well triangle (Figure 3). Ambient groundwater is derived from samples taken from the monitoring wells which are situated outside the production well triangle. The monitoring wells have filter screens at different depths (see Table 2 and Table 3) and the source water was monitored in pond 3.

 Table 1-2:
 Monitoring well ID and filter screen depth of impacted water monitoring wells (location shown in figure 2; data source BWB).

Monitoring well ID	Filter screen depth (mbgl)
TEG357	22.5 – 25.5
TEG218UP	32-34
TEG368UP	12-14
TEG368OP	12-14
TEG364	5-7

mbgl = meter below ground level



 Table 1-3:
 Monitoring well ID and filter screen depth of ambient water monitoring wells (location shown in figure 2; data source BWB).

Monitoring well ID	Filter screen depth (mbgl)
TEG342	18.4-19.4
TEG348	9.55-38.55
TEG332	6.8-15.5

mbgl = meter below ground level

Table 1-4:	Classification	and	overview	of	MAR	techniques
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Parameter	Value/desciption
Enhanced storage	Approx. 12.000.000 m ³ /year*
Horizontal aquifer passage	Shortest distance: 100 m*
Average infiltration rate	0.5 – 4 m/d*
Average injected or infiltrated volume	approx. 9 Mm3/a for all 3 basins (data from 2000-2010)*
Average abstracted volume	8.98 Mm3/a for Saatwinkel well field + 11.65 Mm3/a for Hohenzollern well field (data from 2006)**
Number of basins	3*
Infiltration area	8460 m2 + 8450 m2 + 8700 m2*
Source water type	Lake water (influenced by treated effluent (17-35%))***
Pre-treatment	Settling + micro strainer, pore dia 28µm *

* Möller et al. (2011) based on data from BWB; ** Möller and Burgschweiger (2008) based on data from BWB; ***Ziegler (2001)

Total annual abstraction from all wells in the well triangle is about 21 Mio. m3/a (Möller and Burgschweiger, 2008) and more than two times higher than infiltrated water volumes (Table 4). Apart from the infiltrated water from the recharge ponds, the well field also receives bank filtrate from the Tegel Lake and Upper Havel River (Pekdeger et al., 2006). From these data it can be concluded that the recovery rate for infiltrated pond water is 100 %.





Figure 1-4: Semi schematic cross section between recharge pond, selected impacted water monitoring wells, production well and ambient groundwater wells (Saatwinkel well field) (Pekdeger et al., 2006).

At the recharge site the quaternary sediments consist mainly of fluvial and glacio-fluvial unconsolidated deposits. The aquifer is divided by discontinuously occurring glacial till layers of up to 5m thickness (Figure 4). At the recharge site the upper and lower aquifers are in hydraulic contact to each other (Pekdeger et al., 2006) and form a single hydrogeological unit.



1.2.1.1 Characterization of MAR flow regime (recovery rate, travel times, hydraulic impact zone)

1.2.1.2 General flow field/share of recharged water

In order to determine mixing proportions between source water and ambient groundwater environmental or anthropogenic tracers are often used. The ideal tracer is either of natural or anthropogenic origin, widely distributed in the regarded system, easy to detect and the geochemical behavior is conservative (non-reactive and non-retarding) or at least predictable. Considering a two end-member mixing of the abstracted water between the i) source water and the ii) ambient water the calculation of mixing fraction of recharge water in groundwater or recovered water is:

$$f = \frac{C_r - C_g}{C_i - C_g} \times 100$$
 eq. 1

where:

f = fraction of recharge water present in the well water sample (as percentage)

Cr = tracer concentration in the well water

Cg = tracer concentration in the ambient groundwater

Ci = tracer concentration in the source water

The share of surface water in the individual production wells was determined by Pekdeger et al. (2006) using stable isotopes (δ 180, δ D). An example of mixing calculation is shown in Figure 5.

At the recharge pond in Berlin Tegel the production wells in the eastern part of the well triangle are likely to be influenced by ambient groundwater and recharged water from the pond, while the production wells situated at the northern part of the well triangle are a mixture of the Tegel Lake water and the pond water (Pekdeger et al., 2006). Wells in the southern part of the triangle may contain proportions of groundwater which originates from the Havel River located > 1 km west flowing below the Hohenzollernkanal (Pekdeger et al., 2006).



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Figure 1-5: Proportion of recharge water (surface water) in the abstraction wells (modified from Pekdeger (2006)).

Water from the production wells close to the recharge basins (e.g. well 20) consists on average of 80-90% of recharged water (Pekdeger et al., 2006), while the wells in the northern corner of the well triangle abstract a higher share of ambient groundwater. Groundwater abstraction greatly exceeds the water volumes recharged by the infiltration ponds (see Table 4). Wells in the northern well field receive both water from Tegel Lake and from the recharge ponds. Frequent pumping at the well triangle causes a constant cone of depression, which induces lateral groundwater flow from all sides towards the well triangle. The average travel time from the pond to the production well 20 is given with ~50 days (Pekdeger et al., 2006).



Based on calculation (eq.1) with the two isotopes (δ 18O, δ D) the average proportion of source water in impacted water for all monitoring wells within the production triangle is approx. 98 - 99 % (Table 5). Therefore, groundwater in the well triangle up to a depth of 34 mbgl (maximal filter depth of impacted water monitoring well; see Table 2) consists virtually only of source water.

 Table 1-5:
 Approximation of the proportion of source water in impacted water based on stable isotopes (given in mean isotope ratios).

Tracer	source water (n=26)	impacted water (n=30)	ambient groundwater (n=10)	Proportion of source water in impacted water (%)
δ18Ο	-6.25	-6.24	-7.57	99
δD	-49.15	-49.29	-56.49	98

1.2.1.3 Infiltration cycles

An infiltration cycle consists of 4 stages and the hydraulic behavior of the infiltration pond is described in detail by Greskowiak et al. (2005) and illustrated in Figure 6 and summarised in Table 6.



Figure 1-6: Infiltration cycle at the Berlin Tegel MAR site (modified from Greskowiak et al. (2005).



 Table 1-6:
 Brief description of hydraulics during infiltration cycle in Berlin Tegel (summarized from Greskowiak et al. (2005)).

Stages during infiltration cycle		Description	Approximate duration (days)
Stage 1		steady increase of water saturation until full saturation beneath the pond	10
Stage 2	Early	saturated conditions prevail infiltration rate between 3.5 to 2 m/d	30
Late saturated conditions prevail but sharp decrease of infiltration rate to 0.3 m/d		20	
Sta	ge 3	unsaturated conditions prevail groundwater table dropped to approximately 5 - 6 m below the pond no recharge during late phase	40

If the infiltration rate for a given basin decreases to 0.3 - 0.5 m/d or at least three times a year the basin will be cleaned (Greskowiak et al., 2005; Möller et al., 2011). Cleaning is initiated by interrupting the inflow to the basin. After a drying period of a few days the clogged sediments from the basin up to a depth of 10 cm will be removed and washed (Greskowiak et al., 2005). After washing the sediments is refilled to the basin and distributed over the whole basin.

1.2.1.4 Hydraulic impact zone

The spatial extent of the hydraulic impact zone can be calculated by the empirical formula according to Sichardt (1928):

 $r = 3000 \times s \times \sqrt{k}$ eq. 2

where:

r = radius of the depression cone (m); s = drawdown in the production well (m); k = hydraulic conductivity (m/s) (please note: empirical formula is not unit conform!!!)

The recharge ponds in Berlin Tegel are surrounded by several production wells. The production wells are in distances of 50-100 m to each other and each cone of depression interferes with the neighboring depression cone. The resulting total drawdown in the production well is then used for s. Total drawdown is assumed to be 3-4 m (k = $6.05 \times 10-4$ m/s) and the hydraulic impact zone is then approx. 220 - 295 m around the well triangle. Ambient groundwater monitoring wells are therefore all situated within the hydraulic impact zone.

1.2.2 Characterization of MAR groundwater quality impacts

1.2.2.1 Hydraulic impact zone

How to distinguish between natural and anthropogenic groundwater?

Basically three methods are available to distinguish between natural and anthropogenic groundwater composition: i) statistical component separation (Kunkel et al., 2004), ii) data pre-selection (Mueller et al., 2006) and iii) historical data analysis (Grifficen et al., 2008).

For the component separation method the measured concentration frequency distribution of a chemical compound is separated in statistical components. The underlying concept is that the observed concentration frequency distribution is a result of the superposition of two components: the natural and the influenced component (Figure 7). Both distribution functions can be determined by statistical expressions (amplitude, median and variance), which are fitted by standard algorithms to the observed distribution function. After calibration, the upper and lower threshold of the respective component is then expressed by confidence intervals (usually 10th and 90th percentile).





Figure 1-7: Separation of natural and anthropogenic influenced component from observed concentration distribution (Müller et al., 2006).

Müller et al. (2006) discusses pros and cons of this statistical approach and states that this method provides a sound scientific approach, but is not easy to use for non-experts.

The pre-selection method is based on the idea that certain chemical compounds can be used as tracers indicating exclusively anthropogenic influence. When these substances are detected or exceed certain thresholds the groundwater sample is regarded as anthropogenically influenced and excluded. Tracers are e.g. pharmaceuticals and pesticides which are exclusively of anthropogenic origin or tracers which usually occur in very low concentrations (i.e. nitrate, heavy metals). After the selection procedure, the upper and lower threshold of the regarded compound is then expressed by confidence intervals (usually 10 and 90 percentile). In Müller et al. (2006) pros and cons of the pre-selection approach is discussed. The authors state that this approach tends to exclude more samples than necessary. This method was further developed by the EU research project BRIDGE and proposed as the best procedure to obtain natural background levels for groundwater in Europe (Wendland et al., 2008).

The historical data analysis method is based on the idea that hydrochemical data analysed before a certain time (e.g. before World War II) represents near natural groundwater composition and can therefore be considered as natural background level. Historical chemical composition can either be obtained by hydrochemistry analysed many decades ago or by sampling and analysis of several decades old groundwater. Griffioen et al. (2008) argues that the historical data based on "antique" analysis is the most direct method to assess NBL's. The disadvantages of this method are, amongst others, water conservation errors during sampling for redox sensitive compounds and that analyses are unlikely to be available for many trace elements (Griffioen et al., 2008). Moreover, it cannot be excluded that this "antique" data is in no way influenced by anthropogenic impacts (Griffioen et al., 2008). For a more detailed discussion of advantages and limitations of the different methods we refer to Griffioen et al. (2008).

1.2.2.2 Natural and anthropogenic groundwater in Berlin

In Berlin FUGRO and HYDOR (2002) distinguished between the natural and anthropogenic component in groundwater based on the pre-selection approach. The authors used selection criteria such as high salinity



or presence of organic trace compounds to exclude samples. The resulting selection was then classified according to threshold values from the neighboring state of Brandenburg into natural and anthropogenic groundwater types. Threshold values are given for electrical cond., pH, TOC, Ca, Mg, Na, K, NH4, Fe, Mn, Cl, SO4, HCO3, NO3, NO2, PO4, B, Al for hydrostratigraphic units (aquifer wise) in 10th and 90th percentiles. For our study the threshold values (natural and anthropogenic) for the upper, shallow aquifer (Grundwasserleiter GWL 1) were used and compared with the measured concentrations from the MAR site.

A second study from Reinhardt and Hannappel (2003) regionalized eight parameters (electrical conductivity, SO4, Cl, NH4, K, chemical oxygen demand, PO4 and B) for the upper aquifer in Berlin based on a geostatistical interpolation method. After evaluation and omitting unreliable datasets the arithmetic mean of the respective parameter at the respective monitoring well is used for regionalization based on ordinary kriging. The concentration variance to distance relationship was analysed by variograms before regionalization. In this study it was not intended to differentiate between natural and anthropogenic background values and the results must be considered as the anthropogenically influenced background values. Anyhow, the good spatial resolution provides an additional reference for our study.

1.2.3 Comparison of qualitative data from the Berlin Tegel MAR site with natural and anthropogenic background values

Observed concentrations of major ions and physico-chemical parameters are compared with natural and anthropogenic values from FUGRO and HYDOR (2002) by box and whisker plots. The length of the box shows the 25th and the 75th percentile of the respective dataset. The median is indicated by the line in the box and the arithmetic mean is shown as a rectangle. The whisker indicates the 10th and 90th percentile. Minimum and maximum is indicated by small horizontal lines. Data which is used in this report was measured during the NASRI project and covers a time period from 2001 - 2004 (Heberer and Jekel, 2006; Jekel, 2006; Lopez-Pila and Szewzyk, 2006; Pekdeger et al., 2006).

1.2.3.1 Reliability check and pre-treatment

Before the hydrochemical database is used for interpretation a reliability check is performed in order to ensure a robust database. The amount of cations and the amount of anions with consideration of their valences should be balanced. The hydrochemical analysis of the major ions, given in mg/L, were transformed to mmol(eq)/I or meq/I and the ion balance was calculated according to DVWK (1992) :



$$balance (\%) = \frac{\Sigma \ cations - \Sigma \ anions}{0.5 \times (\Sigma \ cations + \Sigma \ anions)} \times 100 \qquad eq. 3$$

Ion balances above 10% are considered as not reliable. Figure 8 shows all measured samples for source-, impacted and groundwater. All samples are within the tolerance limits.



Figure 1-8: Ion balances for source water, impacted water and groundwater.

Measured concentrations below limit of quantification (LOQ) where set to half of the detection limit of the respective parameter whenever LOQ was available.

1.2.3.2 Major ions and physic-chemical measurements

The electrical conductivity of water is a function of the concentration of dissolved ions. It comprises the solute of inorganic salts (principally calcium, magnesium, potassium, sodium, bicarbonates, chlorides and sulfates) and small amounts of organic matter that are dissolved in water (WHO, 2006). In groundwater, the major part of the ions originates from natural sources (solution of salts, water- rock interactions, mixing etc.) or anthropogenic sources like seepage of agricultural runoff or urban wastewater.



Reinhardt and Hannappel (2003) discusses the variation of electrical conductivity in Berlin groundwater. The authors state that according to Schleyer and Kerndorff (1992) electrical conductivities > 840 μ S/cm are considered as anthropogenically influenced. However, Kunkel et al. (2003) considers values up to 1000 μ S/cm and FUGRO and HYDOR (2002) values between 352 to 608 μ S/cm as natural background values. The spatial distribution of the electrical conductivity in Berlin shows high values in the densely populated city center (\geq 1000 μ S/cm) and low values (\leq 750 μ S/cm) in forested areas (e.g. Tegel forest). The influenced background electrical conductivity of groundwater in the area of recharge is in the range of 750-1000 μ S/cm (Reinhardt and Hannappel, 2003).



Figure 1-9: plots of electrical conductivity and pH from source, impacted and ambient groundwater compared with anthropogenic and natural background values.

At the MAR site source water (median = 680 μ S/cm) and impacted water (median = 730 μ S/cm) is substantially lower mineralized than the ambient groundwater (median = 920 μ S/cm) and impacted water shows higher electrical conductivity than source water (Figure 9). This increase of mineralization is commonly observed during MAR, since the recharge is associated with mineral dissolution. Median ambient groundwater mineralization is within the range of the anthropogenic background values from FUGRO and HYDOR (2002). However, considering the fact that forested areas in Berlin typically show values \leq 750 μ S/cm (Reinhardt and Hannappel, 2003), it cannot be excluded that the mineralization of ambient groundwater due to MAR activities in Berlin Tegel was increased (e.g. by mineral dissolution) in the hydraulic impact zone. The pH decreases from source water (median = 8.1) to the impacted groundwater (median = 7.5) and further to the ambient groundwater (median = 7.2) as shown in Figure 9. Observed range in pH values of the ambient groundwater is within the proposed natural background values.

Major anions of source, impacted and ambient water are displayed by their concentration (mg/l) in Figure 10. In most of the cases source- and impacted water on the one hand and ambient groundwater on the other hand shows distinctly different ion concentration. Compared to source and impacted water the ambient groundwater shows higher concentrations of HCO3, SO4 and Ca. Cl, K and Na reach lower concentrations in the ambient groundwater, whereas Mg concentrations are similar.



Figure 1-10: Box plots of major ions (Cl, SO4, Mg, Ca, HCO3, Na, K) from source, impacted and ambient groundwater compared to anthropogenic and natural background values.

Chloride concentrations in the range of 14-95 mg/l are considered to be general anthropogenic background values in Berlin groundwater (Reinhardt and Hannappel, 2003). At the area of recharge background values for chloride are in the range of 20-50 mg/l (Reinhardt and Hannappel, 2003). Chloride concentration in source water (median = 51 mg/l), impacted water (median = 57 mg/l) and ambient groundwater (median = 41 mg/l) are elevated compared to the natural background values, but within anthropogenic values.

Reinhardt and Hannappel (2003) showed that anthropogenic background values for sulfate concentrations typically found in Berlin groundwater are rarely below 100 mg/l. The authors argue that the sulfate is

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originated from diffusive sources of gypsum. The gypsum is a testimony of the destruction of buildings during the Second World War. Huge areas of the city were destroyed and during the reconstruction of the city the war debris was dumped wherever it was possible. Hence, high concentrations of sulfate (> 360 mg/l) are found nowadays in the densely populated city center (Reinhardt and Hannappel, 2003). At the recharge site background concentration are in the range of 50-120 mg/l (Reinhardt and Hannappel, 2003). Measured concentrations in source water (median = 121 mg/l), impacted water (median = 123 mg/l) and ambient groundwater (median = 227 mg/l) are within anthropogenic background values according to FUGRO and HYDOR (2002). However, the median concentration in the ambient groundwater of 227 mg/l appears to be strongly elevated compared to local anthropogenic background values according to Reinhardt and Hannappel (2003).

Ranges for natural and anthropogenic magnesium background concentrations show a wide overlapping zone (Figure 10). Magnesium concentration in source, impact and ambient groundwater are similar and plot within the ranges of the natural and anthropogenic background concentrations.

Calcium and HCO3 concentrations in the ambient groundwater are elevated compared to source and impacted water, but within ranges of anthropogenic background values.

Sodium concentrations in source and impacted water are elevated compared to the ambient groundwater but are within the anthropogenic background values and above natural background. The high proportion of treated effluent increases the sodium concentration in source water (Massmann et al., 2004).

General anthropogenic background concentrations of potassium in Berlin groundwater is given with 3-4 mg/l, while local background values are between 6-12 mg/l (Reinhardt and Hannappel, 2003). Both sourceand impacted water are within the concentration ranges of local background values according to Reinhardt and Hannappel (2003), but exceed natural background values according to FUGRO and HYDOR (2002). Median concentration of ambient groundwater (4.5 mg/l) is similar to natural background values.

Except for K and Mg all other major ion concentrations in the ambient groundwater exceed proposed natural background levels, but are within anthropogenic values typically found in Berlin's shallow groundwater. Still, especially SO4, Ca and HCO3 are at the upper edge of anthropogenic threshold values and may indicate an impact of MAR activities on ambient groundwater. As shown above, monitoring wells for the ambient groundwater are all situated within the hydraulic impact zone of the MAR site. Groundwater table fluctuations due to pumping introduce oxygen to the hydraulically impacted zone and the entrapped air is dissolved subsequently during stages of groundwater table rise and thereby oxidizing finely distributed Fe-sulphides commonly present in the sediments (Pekdeger et al., 2006). Oxidation releases acidity and would lead to additional calcite dissolution. These processes may lead to the observed lowered pH in the ambient groundwater and the elevated SO4, Ca and HCO3 concentrations.

1.2.3.3 Inorganic trace elements

Inorganic trace elements (Fetot, Mn, B) are displayed by their concentration (mg/l) in Figure 11 and compared to background values. The median concentrations of Fe and Mn in the source and impacted water are generally lower than in the ambient groundwater. Greskowiak et al. (2005) discusses the spatial and temporal changes in redox zonation at the site and states that the redox zonation at the recharge



pond(s) is controlled by the transient hydraulic behavior of the system. Redox conditions below the infiltration pond are dominated by oxic conditions, but sub-oxic conditions develop especially in deeper part of the aquifer reaching Fe-reducing conditions (Greskowiak et al., 2005). The measured Mn/Fe concentrations in the impacted water are low and mostly below detection limit (Fe = 0.03 mg/l and Mn 0.005 mg/l). This is explained by rapid precipitation of amorphous Fe(OH)3 (Greskowiak et al., 2005). In the ambient groundwater Fe and Mn concentrations are elevated but within the natural ranges.



Figure 1-11: Box plots of inorganic trace elements (Fetot, Mn, B) from source, impact and ambient groundwater compared with anthropogenic and natural background values.

Boron is commonly used as a washing powder additive, not eliminated completely during wastewater treatment (Massmann et al., 2004) and used at the site as a tracer substance to identify mixing processes (Wiese et al., 2011). Boron concentrations in source, impacted and ambient groundwater are similar and within anthropogenic background values.



1.2.3.4 Nutrients

Data of NO3, NH4 and TOC for source water, impact- and ambient groundwater is shown in Figure 12. As for DOC no background values exist, measured PO4 concentrations are not available and NO2 was never detected, these parameters are therefore not shown.

When NH4 occurs in high concentrations in the water cycle, it is usually an indicator for untreated sewage, agricultural runoff or landfill leakage. It is only measured in anaerobic water because in the presence of oxygen it is converted to nitrite (NO2) and in a second step to nitrate (NO3) by microbiological oxidation (nitrification). The observed concentrations of N-species (NO3, NH4) at the MAR site are generally low. Nitrate (NO3) is elevated in source- and impacted water compared to ambient groundwater. The highest concentrations of NO3 can be found in the impacted water. Measured NO3 concentrations in the ambient groundwater are within the ranges of natural background values. NH4 is virtually not present in source water (median = 0.09 mg/l) and impacted water (median 0.12 mg/l, but with very low number of measurements n=3). Only in the ambient groundwater elevated median concentration of 0.66 mg/l can be observed, but are in the range of anthropogenic background values.

TOC is highest in source water (median = 7.7 mg/l) and lowest in impacted water (median = 5 mg/l). Measured DOC concentrations (not shown here!) are very similar to measured TOC, but slightly lower. A decrease of TOC in the source water compared to the impacted water is commonly observed during MAR. The biodegradable proportion of organic carbon is consumed by microorganisms, coupled to the reduction of terminal electron acceptors, such as O2, NO3, Mn, Fe.

Median concentration of measured TOC in source and ambient groundwater exceeds natural as well as anthropogenic background values, only the impacted water is within the anthropogenic background





Figure 1-12: Box plots of nutrients in source water, impacted- and ambient groundwater compared with anthropogenic and natural background values.

1.2.3.5 Microbiology

The indicator microorganisms, Escherichia coli, intestinal enterococci, and coliphages measured in the source water, impacted water and in the ambient groundwater are shown in Table 7. Coliphages were found in the source water in concentrations between 2 and 26 pfu/100 ml, but not in the ambient groundwater samples. Concentrations of intestinal enterococci in pond water varied between 1 and 5 cfu/100ml and were not detected in ambient groundwater samples. E.coli was detected in the source water in concentrations up to 44 cfu/100 ml (average 13 cfu/100 ml) and was also found in the ambient groundwater but not in the impacted water.

Table 1-7:	Occurrence of somatic coliphages (pfu/100 ml), intestinal enterococci (cfu/100ml), E. coli (cfu/100 ml)
	in source, impacted and ambient groundwater samples (average concentration).

Microoganism	unit	Source water	Impacted water**	Ambient groundwater

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Somatic coliphages*	pfu/100 ml	11 (n=5)	<1 (n=10)	< 1 (n=5)
Intestinal Enterococci*	cfu/100 ml	2 (n=5)	<1 (n=10)	<1 (n=5)
E.Coli*	cfu/100 ml	13 (n=5)	2.2 (n=10)	10 (n=5)

*data from Lopez-Pila et al. (2011), detection limit: 1 pfu/100 ml; for colony counts 1 cfu/ml; **samples taken from shallow monitoring well TEG365 and TEG366, please note: monitoring wells not shown in figure 2

The results of the microbiological investigations indicate a comparably high hygienic quality of the source water at the recharge pond in Berlin-Tegel (Lopez-Pila et al., 2011). However, the authors state that during sampling secondary contamination, e.g. through not sterilized sampling equipment, cannot be ruled out completely and the source of the E.coli detection in the ambient groundwater remained unclear (Lopez-Pila et al., 2011).

Legislation of some countries with MAR systems assumes that an underground passage lasting, depending on the country, around 50 days will be free of pathogens (DVGW, 2006). Furthermore, assuming that the detection of E.coli in the ambient groundwater was caused by secondary contamination during sampling and the high recovery rate of infiltrated water by the surrounding production wells, it can be concluded that microbial contamination of the ambient groundwater by the MAR activities is very unlikely. However, considering the low frequency of measurements and low number of organisms it is recommended to improve the baseline data.

1.2.3.6 Organic trace compounds

Massmann et al. (2006) investigated the fate and transport of a wide range of organic trace compounds during bank filtration in Berlin. The authors state that "WWTPs (Wastewater treatment plants) receive a large spectrum of organic contaminants which are partly eliminated during treatment (Heberer, 2002a; Ternes, 1998), but several persistent organic contaminants are not removed. Adsorbable organic halogens (AOX) are, for example, present in the lake (Grünheid et al., 2005; Ziegler et al., 2002). Concentrations of anthropogenic Gadolinium (Gd), which is brought in as a contrast agent (Gd-DTPA), are strongly elevated (Bau and Dulski, 1996; Knappe et al., 2005). A number of pharmaceutically active compounds (PhACs) such as clofibric acid, diclofenac, ibuprofen, phenazone, propyphenazone, primidone and carbamazepine are not eliminated completely during the WW treatment process and have been detected in the surface water (Heberer, 2002a; Heberer et al., 2004; Reddersen et al., 2002; Zühlke, 2004)."

Pekdeger et al. (2006) described the different sources of organic trace compounds in the area of the recharge ponds. The authors state that: "While highest phenazone and AMDOPH concentrations are found in the south-west, highest propyphenazone (analgesic/anti-inflammatory) concentrations are found in the



south-west and in the north, towards Lake Tegel. The phenazone-type pharmaceuticals and related substances originate from the surface water, where their presence is caused by their discharge from WWTP (Heberer, 2002a) or from former production spills of a pharmaceutical plant near Oranienburg on the Upper Havel, which produced phenazone-type pharmaceuticals. Reddersen et al. (2002) suspected that spills of the plant released into the environment in the past, when regulations were less strict, are the cause of some of today's findings of PhAC residues. Because of the pharmaceutical plant, phenazone and dimethylaminophenazone (not detected) concentrations in the surface water of the Upper Havel were probably considerably higher in the past decades than they are today (exact values are not known). In addition, the production of dimethylaminophenazone was stopped in 1978 (Reddersen et al., 2002). Therefore, the high concentrations of phenazone and AMDOPH in the south-west indicate that the groundwater is probably older bank filtrate (similar to findings in greater depth at the bank filtration transects, where high phenazone and AMDOPH concentrations always corresponded to an older age of the bank filtrate). It infiltrated from the Upper Havel 1-2 km further west, passed the industrial contamination sites (thereby accumulating As, MTBE etc.) and is now abstracted by the production wells with a considerable time lag of a few years to a few decades. In addition, it appears that the share of "older" BF containing phenazone and, in particular, AMDOPH is getting larger with depth at all investigated sites (Figure 13)."







Figure 1-13: Spatial disctribution of Phenazone-type pharmaceuticals and residues phenazone, AMDOPH & propyphenazone (Pekdeger et al., 2006).

The authors summarized the main input paths for contaminants and water constituents as illustrated in Figure 13.



Figure 1-14: Major input paths for various water constituents in the area of the recharge ponds (Pekdeger et al., 2006).

Consequently, organic trace compounds are introduced by source and ambient groundwater to the MAR site in Berlin-Tegel. During the DEMEAU project ten priority substances were identified. The selection is based on the following criteria:

- Commonly found in wastewater / drinking water supplies
- Environmental relevance
- Broad spectrum of chemical and physical properties
- Covering a wide range of elimination potential
- Existence of analytical methods

Out of these substances only for Carbamazepine, Phenazone, Bezafibrate, Primidone and Diclofenac data was available. Additionally, AMDOPH was selected because of the local importance.

Carbamazepine is a drug primarily used for treatment of epilepsy and enters the environment through incomplete removal in WWTPs (Heberer, 2002b). Carbamazepine occurs in the Berlin's surface water with maximal measured concentration of 1.87 μ g/l (Adam, 2010). The measured maximum concentration in the source water was observed to reach almost 1 μ g/l. In the ambient groundwater carbamazepine is mostly

below the limit of quantification (LOQ), but found two times above the LOQ. Removal of Carbamazepine during subsurface passage is considered to be limited and seen as relatively persistent (Massmann et al., 2006). Consequently, Carbamazepine is introduced by source water, removed only marginally during subsurface passage and abstracted by production wells (further concentration decrease by dilution).

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Figure 1-15: Box plots of Carbamazepine, Phenazone, AMDOPH, Bezafibrate, Primidone and Diclofenac (LOQ = limit of quantification).

The fate of the pharmaceutical residue Phenazone was investigated by Greskowiak et al. (2006) in detail at the MAR site in Berlin-Tegel. The authors found that Phenazone breakthrough at monitoring wells within the well triangle were governed by warmer temperatures when anaerobic redox conditions developed. In winter, when aerobic conditions prevail, no breakthrough was observed. Hence, at the recharge site Phenazone is not completely removed during subsurface passage (Figure 15). In the ambient groundwater Phenazone is mostly below the LOQ, but detections above LOQ are explained to be originated from production spills of a pharmaceutical plant at the Upper Havel decades ago (Pekdeger et al., 2006).

The metabolite AMDOPH is measured in the Berlin surface water with maximum concentration of 5.3 μ g/l (Adam, 2010). In Berlin drinking water it was measured with 3 μ g/l (Reddersen et al., 2002). AMDOPH concentrations in ambient groundwater concentration show large variations and are also associated to be originating from production spills of a pharmaceutical plant at the Upper Havel River (Pekdeger et al., 2006).

Bezafibrate is detected only in source water, but mostly below LOQ. Impacted water and ambient groundwater is not affected by Bezafibrate.

The antiepileptic primidone occurs ubiquitarily in the Berlin water cycle and was measured in concentrations of up to $1.55 \ \mu g/l$ in Berlin's surface water (Adam, 2010). At the recharge site primidone is detected in the impacted water in similar median concentrations compared to source water. Ambient groundwater concentrations are lower, but above LOQ. Sources of primidone in ambient groundwater are unknown.

Diclofenac is occurring at maximum concentrations of 2.36 μ g/L in Berlin's surface water (Adam, 2010). In the ambient groundwater at the Tegel site concentrations are always below LOQ. Compared to source water concentrations the impacted water concentrations are decreased and show a substantial removal during underground passage.

Among the selected organic trace compounds primidone, phenazone and phenazone-type metabolite AMDOPH are of relevance because of elevated concentration. Phenazone and AMDOPH are suspected to be originated from the Upper Havel River and transported as bankfiltrate to the MAR site. Primidone was found to be persistent during several studies (Heberer, 2002a; Heberer et al., 2004) and is also detected in the ambient groundwater.

1.3 Summary and conclusions

This report assesses the impact of MAR on ambient groundwater in terms of hydraulic and water quality influences. Impact zones of MAR structures were divided into a) hydraulic impact zone and b) attenuation zone. Different transport processes of compounds during e.g. pond infiltration are schematically shown and explained. Within this report water quality data from one MAR site in Berlin Tegel are compared with natural and anthropogenically influenced background values in the aquifer. Common approaches to determine background values in groundwater are introduced and described. At the MAR site in Berlin-Tegel water quality parameter were observed in the infiltration pond (source water), in observation wells between the ponds and the production wells (impacted groundwater) and beyond the recovery wells (ambient groundwater). After hydraulic characterisation of the MAR site observed concentrations of major ions, physico-chemical parameters, inorganic trace compounds, nutrients and organic trace compounds were compared with natural and anthropogenic background values (if any) by statistical plots.

The recharge site in Berlin-Tegel is characterized by highly transient infiltration rates between 0.3-4 m/d, relatively short travel times of recharge water to the production well (~50 days) and seasonally changing redox conditions (oxic to Mn/Fe reducing) during subsurface passage. The share of recharged water in the production wells varies between 20 - 90 % and the recovery rate of infiltrated water is considered to be 100 %. The hydraulic impact zone was approximated to be 220 - 295 m around the production wells. Distance from the infiltration pond(s) to production wells varies between 100 - 400 m.

Source water (=pre-treated surface water from Lake Tegel) and ambient groundwater differ substantially in their major hydrochemical composition. Ambient groundwater is elevated in HCO3, SO4 and Ca and depleted in Cl compared to source water. Except for K and Mg all other major ion concentrations in the ambient groundwater exceed proposed natural background levels, but are within anthropogenic values



typically found in Berlin's shallow groundwater. Especially SO4, Ca and HCO3 are at the upper edge of the range of anthropogenic threshold values and may indicate an impact of MAR activities on ambient groundwater. Groundwater table fluctuations due to pumping introduce oxygen to the hydraulically impacted zone and the entrapped air is dissolved subsequently during stages of groundwater table rise, thereby oxidizing Fe-sulphides commonly present in the sediments (Pekdeger et al., 2006). Oxidation releases acidity and would lead to additional calcite dissolution. These processes may lead to the observed lowered pH in the ambient groundwater and the elevated SO4, Ca and HCO3.

In the ambient groundwater Fe and Mn concentrations are elevated but within the natural groundwater ranges. Boron concentrations in source, impacted and ambient groundwater are similar and within anthropogenic background values.

The observed concentrations of N-species (NO3, NH4) at the MAR site are generally low. Nitrate (NO3) is elevated in source- and impacted water compared to ambient groundwater. Median concentration of measured TOC in source and ambient groundwater exceeds natural as well as anthropogenic background values, only the impacted water is within the background values.

Microbial data suggest that microbial contamination of the ambient groundwater by the MAR activities is very unlikely. However, considering the low frequency of measurements and low number of organisms it is recommended to improve the baseline data.

Among the selected organic trace compounds carbamazepine, phenazone, phenazone-type metabolite AMDOPH and primidone are of relevance, as they are not removed completely during subsurface passage in the impacted groundwater. Phenazone and AMDOPH are suspected to be originated from the Upper Havel River, transported as bankfiltrate to the MAR site. Primidone was found to be persistent during several studies (Heberer, 2002a; Heberer et al., 2004) and is also detected in ambient groundwater. Of the selected trace compounds five were present in source water well above LOQ. Three of these showed little degradation during infiltration (carbamazepine, primidone, AMDOPH), while two (phenazone, diclofenac) showed substantial reduction. Bezafibrate is detected only in source water, but mostly below LOQ. Impacted water and ambient groundwater is not affected by bezafibrate.

This report shows that the MAR site in Berlin-Tegel shows substantial removal of many compounds (please note that total removal observed in the recovery well is higher). Compounds which were found to be persistent are abstracted by the production wells and a water quality impact of the infiltrated source water beyond the attenuation zone is unlikely. However, mobilization of SO4 and Fe by the MAR activity in the hydraulic impact zone cannot be excluded. Special attention must be paid to contaminants transported from the ambient groundwater to the production wells through various sources.



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