



## Pilot plant experiences using physical and biological treatment steps for the remediation of groundwater from a former MGP site

T. Wirthensohn<sup>a,\*</sup>, P. Schoeberl<sup>b</sup>, U. Ghosh<sup>c</sup>, W. Fuchs<sup>a</sup>

<sup>a</sup> University of Natural Resources and Applied Life Sciences-Vienna, Department of IFA-Tulln, Institute for Environmental Biotechnology, Konrad Lorenz Strasse 20, 3430 Tulln, Austria

<sup>b</sup> Wienenergie Gasnetz GmbH, Referat 17-Altlasten, Josefstädterstrasse 10-12, 1080 Vienna, Austria

<sup>c</sup> Department of Civil and Environmental Engineering, University of Maryland Baltimore County, Baltimore, MD 21250, USA

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### ABSTRACT

The production of manufactured gas at a site in Vienna, Austria led to the contamination of soil and groundwater with various pollutants including PAHs, hydrocarbons, phenols, BTEX, and cyanide. The site needs to be remediated to alleviate potential impacts to the environment. The chosen remediation concept includes the excavation of the core contaminated site and the setup of a hydraulic barrier to protect the surrounding aquifer. The extracted groundwater will be treated on-site. To design the foreseen pump-and-treat system, a pilot-scale plant was built and operated for 6 months. The scope of the present study was to test the effectiveness of different process steps, which included an aerated sedimentation basin, a submerged fixed film reactor (SFFR), a multi-media filter, and an activated carbon filter. The hydraulic retention time (HRT) was 7.0 h during normal flow conditions and 3.5 h during high flow conditions. The treatment system was effective in reducing the various organic and inorganic pollutants in the pumped groundwater. However, it was also demonstrated that appropriate pre-treatment was essential to overcome problems with clogging due to precipitation of tar and sulfur compounds. The reduction of the typical contaminants, PAHs and BTEX, was more than 99.8%. All water quality parameters after treatment were below the Austrian legal requirements for discharge into public water bodies.

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## 1. Introduction

### 1.1. Soil and groundwater contamination from gasworks sites

Groundwater contamination by various anthropogenic organic compounds is a widespread problem in industrialized environments [1–5]. Especially former gasworks or manufactured gas plant (MGP) sites are recognized as extensive sources of soil and groundwater pollution [6,7]. Former MGP sites are contaminated with various hydrocarbons derived from by-products such as tars and other residues that were often stored and/or disposed of at such facilities. Typically contaminants include polycyclic aromatic hydrocarbons (PAHs), BTEX, phenols and various inorganic contaminants [8–12].

### 1.2. Approaches for remediation of MGP sites

Remediation of former MGP sites typically comprises activities for source removal or control and for the cleanup of contaminated groundwater. With regard to cleanup efficiency, it is clearly advisable to remove the core contamination from the subsurface if that is possible. However accurately localizing non-aqueous phase liquids (NAPLs) in the subsurface may be very difficult [13]. Excavation and subsequent ex situ treatment are very expensive techniques. The extracted soil has to be washed, treated thermally, or else safely disposed. The costs for hazardous waste landfills have been increasing. Therefore more economical methods are favored such as pump-and-treat, in situ thermal desorption, biological treatment, and water-based soil washing [13]. Other techniques aimed at volatilization of organic contaminants from soils (e.g. steam stripping or vapor extraction) are not expected to be effective for removal of the high molecular weight, low volatility tars encountered at MGP sites [13]. Generally, ex situ techniques are more costly and cause a severe disruption of the environment. Sometimes ex situ techniques cannot be applied if access to the contaminated soils is limited due to existing structures.

\* Corresponding author. Tel.: +43 2272 66280 555; fax: +43 2272 66280 503.  
E-mail address: [thomas.wirthensohn@boku.ac.at](mailto:thomas.wirthensohn@boku.ac.at) (T. Wirthensohn).

Groundwater pollution causes further migration of contaminants and is of concern due to the potential impact of contaminating drinking water supplies over a large area [14]. Plumes of contaminants can extend 0.5–10 km from their source, even though the migration of the contaminants is slower than the groundwater velocity. These plumes form over decades and are common in North America and Europe. A series of recovery (extraction) wells or interceptor trenches can be implemented for continuous pumping of contaminated groundwater. In addition, monitoring wells and injection wells for infiltration may be necessary. This provides hydraulic control of subsurface contaminants to prevent their migration [15]. The contamination concentration of the extracted water often decreases initially, followed by a leveling of concentration and sometimes a gradual decline, which is generally expected to continue over decades [13]. This is due to the slow desorption and dissolution of certain contaminants (especially heavy components in NAPLs) in groundwater. Another limitation is, that the groundwater flows mainly in the high-permeability zones, while the low-permeability layers and lenses are flushed less effectively [16]. These mass transfer limiting processes result in long pumping times [17]. Projected time frames for pump-and-treat operations range from 10 years [18] to longer than 100 years [13]. In the case of former MGPs, remediation involving pump-and-treat has to be considered more as a hydraulic control than a complete remediation process [13,16,17,19–21]. Therefore pump-and-treat is conveniently combined with other remediation techniques.

### 1.3. Pump-and-treat concepts

The traditional pump-and-treat system comprises a series of recovery (extraction) wells or interceptor trenches to pump the contaminated groundwater from the subsurface for further remediation in a treatment plant. The mixture of various contaminants in the groundwater at former MGP sites requires several process steps. Typically, treatment involves a combination of physical, chemical, and biological methods, while the particular plant configuration is often site specific [13].

In a study at Griftpark, a gas work site in Netherlands, four different combinations of treatments were investigated. The pre-selection of treatment methods in the plant was based on a theoretical feasibility study in which all available methods were considered and several additional laboratory tests [22]. For initial treatment, stripping technologies were compared to fixed biofilm and activated sludge remediation. This first step was followed by coagulation, flocculation, or sedimentation. All combinations had a sand filtration and an activated carbon filter at the end of the treatment train. Sand filtration is an inevitable step for solids removal, before the activated carbon filter can be applied for final polishing [23].

As a result of the study of different process combinations, biological treatment is recommended as a core element of the treatment concept. Hydrocarbons (HC), especially smaller ones, have proven to be readily biodegradable under aerobic conditions [16]. While activated sludge processes work well for ordinary waste water, fixed biofilm reactors are less sensitive to variations in influent supplies and are also better adapted to groundwater with comparable low concentration of contaminants. The outer layers of the biofilm protect the inner cells from toxicity and reduce soluble contaminant concentration by adsorption [24]. Biofilms provide a high density of microorganisms, also the hydraulic retention time (HRT) can be low while maintaining high cell residence times. Within the different systems using fixed biofilms, submerged upflow fixed-film reactors (SFFRs) have proven to be most successful [12]. Rotating biological contactors with partially immersed disks or trickling filters are less efficient, while the disadvantages of fluidized-bed reactors

are mainly the higher investments costs and the lack of stability [25,26].

In the investigated case, a combination of physical pre-treatment, followed by biological treatment and finally absorption was chosen. A SFFR was employed using expanded clay pellets, commonly known under their brand name Leca, as a biofilm support material. A multi-media filter and granulated activated carbon filters (GACFs) were established at the end of the treatment process. On one hand the GACF absorb substances, which have not undergone removal up to this point; on the other hand they provide a final safeguard in case previous treatment steps would fail.

### 1.4. Aims and scope

In Austria, the remediation of contaminated sites is a legal requirement demanding high standards compared to many other countries [27]. The investigated former MGP site in Vienna, Austria with a size of 325,000 m<sup>2</sup> is situated in a groundwater stream, which is 300 m distance from a river. It was classified as subject to remediation according to Austrian law *Alsag* (Austrian law for abandoned hazardous sites) [27] in 1996. In 2000 it was categorized class 1, giving it the highest priority. During evaluation of the site, samples of 187 bores at different locations and depths were analyzed. The groundwater stream was found to be complex, since the general flow direction (south-east) was interfered by a nearby underground tube. Twenty-one extraction wells were drilled which would be regulated by control wells. Furthermore, three monitoring wells were drilled. All the mentioned bores are downstream of the site.

The objective of the pilot study was to assess options for a full-scale long-term plant, in order to be cost-effective while meeting all environmental obligations. The goal is to make recommendations on which treatment steps have to be implemented in a pump-and-treat system. Most of the treated groundwater will be recycled up-stream of the contaminated site through an infiltration gallery. However, part of the pumped water has to be discharged to ensure hydraulic containment. For discharge of the treated groundwater three different options were considered with increasingly stringent legal standards: (1) discharge into sewerage system, (2) discharge into the adjacent river, and (3) recharge into groundwater. Hence, the principal aims of the study were to (i) examine the performance of the physical and biological treatment steps, (ii) identify problems that occur during treatment plant operation and (iii) determine whether remediation goals may be achieved for discharge of effluent water into a sewer, surface water, or recharge into groundwater.

## 2. Methodology

### 2.1. Groundwater

Two of the mentioned bores exhibiting the highest contamination levels were selected for the pilot plant experiments, one located near the former tar disposal (Well 1), the other one at the former naphthalene scrubber (Well 2). The previous investigations about the groundwater were completed with additional analysis to get a complete picture of the groundwater quality of the two wells, since they differed significantly in composition. An overview of the quality of the groundwater is provided in Table 1. The groundwater had a stable temperature between 13.1 and 13.7 °C and a pH between 6.7 and 7.4 throughout the year.

The groundwater of both wells showed comparable COD concentrations of 21–68 mg/l. The other parameters showed differences, for example, Well 1 had higher concentrations of

**Table 1**  
Groundwater quality and analytical methods

Parameter	Method	Well 1	Well 2
pH	DIN <sup>a</sup> 38 404-5	6.7–7.4	7.1–7.2
Dissolved oxygen (DO) (mg/l)	DIN EN <sup>b</sup> 25814	0.0	0.0
Oxidation reduction potential (ORP) (mV)	ISO <sup>c</sup> 11272	–280 to –380	–260 to –330
Conductivity ( $\mu\text{S}/\text{cm}$ )	DIN 38 404-8	1378–1424	1412–1437
PAH ( $\mu\text{g}/\text{l}$ )	DIN 38407 F8	182–745 <sup>d</sup>	789–865 <sup>d</sup>
Naphthalene ( $\mu\text{g}/\text{l}$ )	DIN 38407 F8	56–128	589–648
Benzo(a)pyrene ( $\mu\text{g}/\text{l}$ )	DIN 38407 F8	<0.03	<0.03
BTEX ( $\mu\text{g}/\text{l}$ )	DIN 38407/9-1 GC	295–635	742–806
Benzene ( $\mu\text{g}/\text{l}$ )	DIN 38407/9-1 GC	247–547	366–512
Phenols (mg/l)	DIN 38 409 H16 1-3	0.21–0.53 <sup>e</sup>	0.04–0.08 <sup>e</sup>
Cyanides (mg/l)	DIN 38405 D13	0.0–0.18 <sup>f</sup>	0.18–0.25 <sup>f</sup>
TOC (mg/l)	DIN EN 1484	4.32–13.0	6.0–6.4
COD (mg/l)	DIN 38409-H 41	21–61	37–68
BOD <sub>5</sub> (mg/l)	DIN 38 409-H51	4.5–12.5	10.5–16.0
HC (mg/l)	EN ISO 9377-2	0.21–1.10	0.32–0.88
NH <sub>4</sub> <sup>+</sup> (mg/l)	DIN 38414	3.2–7.1	3.1–3.9
NO <sub>2</sub> <sup>-</sup> (mg/l)	DIN 26777	<0.01	<0.01
NO <sub>3</sub> <sup>-</sup> (mg/l)	DIN 38405	<0.01	<0.01
Fe <sup>2+</sup> (mg/l)	DIN 38406 E1-1	0.24–0.48	2.7–3.2
Mn <sup>2+</sup> (mg/l)	DIN 38406-33	0.12–0.21	0.35–0.46
S <sub>2</sub> <sup>-</sup> (mg/l)	DIN 38405 D 26	9.9–17.6	3.12–3.48
PO <sub>4</sub> -P (mg/l)	DIN EN 1189	<0.05–0.12	0.05–0.13

<sup>a</sup> DIN standard.<sup>b</sup> European standard.<sup>c</sup> ISO standard.<sup>d</sup> Sum of EPA 16.<sup>e</sup> See comments on phenol analytics in Section 3.2.5.<sup>f</sup> Easily purgeable cyanides.

hydrocarbons, phenols, and sulfur, while Well 2 had higher concentrations of PAHs and BTEX.

## 2.2. Pilot plant design

As described earlier, the pilot plant comprised several treatment steps. The general layout and principal processes of the pilot plant are presented in Fig. 1.

### 2.2.1. Sedimentation/flotation

The sedimentation/flotation was carried out in an open top rectangular basin of 18.10 m<sup>3</sup> volume (L × W × D: 4.6 m × 2.3 m × 2.5 m). It consisted of an influent zone, a settling zone, and a pump chamber separated by baffles. The HRT was 5 h during normal flow condition (1 l/s) and 2.5 h during high flow condition (2 l/s). It turned out that a significant part of the particles do not settle but rather float on the surface. To enhance separation by flotation, the influent zone was equipped with an aeration system after 64 days of operation. Two membrane disc diffuser (Nopon KKI 225; A = 2 × 0.025 m<sup>2</sup>) were installed, producing bubbles of 1–3 mm diameter. The air supply was 1.5–4.0 m<sup>3</sup>/h. Furthermore, a skimmer was installed to continuously remove floating particles while the settled solids were excavated manually on occasion.

### 2.2.2. Submerged fixed film reactors (SFFRs)

Two slightly different SFFRs, termed “BioH” and “BioK”, were installed and operated as parallel systems to investigate different HRTs. BioH had a volume of 1.87 m<sup>3</sup>, BioK had a volume of 1.58 m<sup>3</sup>, hence different HRTs occurred (Table 2). At start-up, the reactors were inoculated using activated sludge. The inoculum was obtained from a waste water treatment plant at an oil refinery, adapted to the treatment of hydrocarbons.

The air supply for the reactors was 2 m<sup>3</sup>/h each. Since the level of dissolved oxygen (DO) in the effluent after 2 months of operation was very high at 9 mg/l, the air supply was reduced to 1.5 m<sup>3</sup>/h. The residual DO of 7 mg/l was still sufficient for aerobic biological

**Table 2**  
SFFR technical data

	BioH	BioK
Height (m)	1.65	1.40
Volume (m <sup>3</sup> )	1.87	1.58
Diameter (m)	1.20	1.20
Height over all (m)	2.18	1.80
Package material	LECA expanded clay pellets (diameter: 6–8 mm)	
Aeration	Tube diffusers; membrane area/reactor = 0.065 m <sup>2</sup>	
Flow regime	Co-current upflow of influent and air	

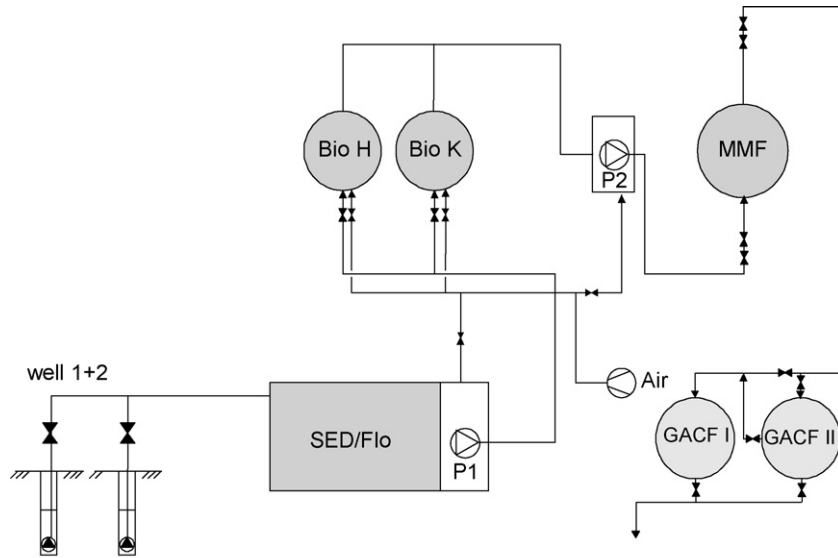
activity. The groundwater flow was split 50:50 to both SFFRs. The resulting HRT in the SFFRs were 1.04 and 0.88 h, respectively, at a flow rate of 1 l/s. Accordingly, at the high flow conditions of 2 l/s HRTs were 0.52 and 0.44 h in the SFFRs.

### 2.2.3. Multi-media filter (MMF)

The technical data of the MMF are summarized in Table 4. In between the SFFRs and the MMF was a storage tank. The pump therein produced the pressure to move the groundwater further on through the MMF (HRT = 0.63 or 0.32 h) and the following GACF (Table 3).

**Table 3**  
Technical data of the multi-media filter (MMF)

Filter height (m)		1.40
Filter volume (m <sup>3</sup> )		2.3
Diameter (m)		1.09
Overall height (m)		1.94
Package material	Particle size (mm)	Layer and thickness (cm)
Hydro anthracite	0.6–1.6	Top: 40
Fine filter sand	0.7–1.3	Upper middle: 40
Coarse filter sand	2.0–3.15	Lower middle: 40
Gravel	5.6–8.0	Supportive layer: 20



**Fig. 1.** Scheme of the pilot plant setup. SED: sedimentation/flotation; BioH, BioK: submerged fixed film reactors (SFFR); GACF I, GACF II: granulated activated carbon filters; MMF: multi-media filter; P1, P2: pumps.

#### 2.2.4. Granulated activated carbon filter (GACF)

Two similar GAC filters were employed to obtain data about the adsorption capacity of activated carbon. (GACF 1: 88 days, and GACF 2: 94 days). It was intended to operate them consecutively. However, due to the excellent effluent quality, only one of them was operated at a time whereas the other one was maintained in a stand-by mode. The volume of the GACFs was 1.5 m<sup>3</sup> each, providing an HRT of 0.42 during standard flow rates and 0.21 h in the high flow state. The diameter of the filter was 1.2 m, sampling ports were at the heights of 1.7, 0.7 and 0.2 m. The carbon used in the GACF were in the form of pellets “Donaucarbon CC50P” (see Table 4).

#### 2.3. Data collection, sampling, and analysis

The pilot plant was controlled by a programmable logic controller (PLC) and data about flow, pressure, temperature and pH were recorded automatically every hour. Samples were taken weekly from the influent, whether Well 1 or a mixture of Well 1 and Well 2 during the high flow stage. Samples were also taken from the process units, described above (SED, Bio, MMF and GACF). The parameters analyzed are listed in Table 1 along with the methods used for analysis.

#### 2.4. Schedule of experiments

Experiments were conducted for 6 months, treating either 1 or 2 l/s with HRT all over the treatment steps of 7 and 3.5 h, respectively. The experimental stages were as shown in Table 5.

**Table 4**  
Supplier data of activated carbon “Donaucarbon CC50P”

Pellet diameter (mm)	3.5–4.0
Mean density (kg/m <sup>3</sup> )	500 ± 50
Ash content (% w/w)	<15
Water content (% w/w)	<5
Iodine absorption (mg/g)	>800
ClC <sub>4</sub> -activity (% w/w)	>40

**Table 5**

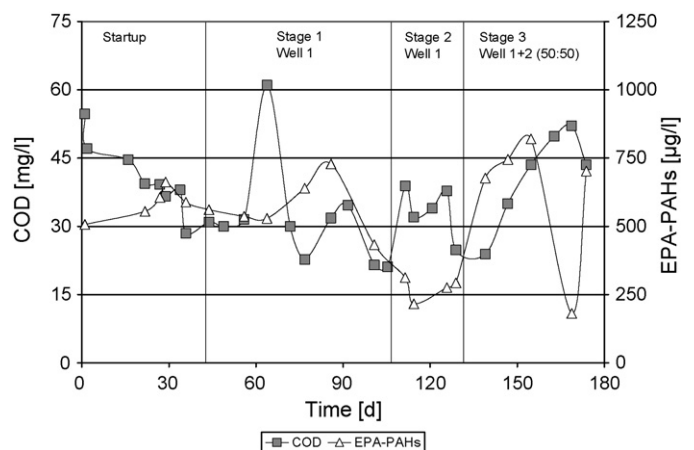
Experimental stages of the pilot treatment plant

Stage	Time, Well
0: start-up	40 days, Well 1
1: standard hydraulic loading rate (flow rate 1 l/s), phosphate dosage	65 days, Well 1
2: standard hydraulic loading rate (flow rate 1 l/s), without phosphate dosage	30 days, Well 1
3: high flow (flow rate 2 l/s)	55 days, Well 1 + Well 2

### 3. Results and discussion

#### 3.1. Development of groundwater quality

In the course of the operation of the pilot plant the concentration of the contaminants showed significant variations in the influent. Fig. 2 shows the development of the COD concentration as a gross parameter of organic compounds and sum of 16 EPA priority pollutant PAHs as one of the main treatment goals. As a general tendency, the COD concentration and all other contaminants decreased slightly during stage 1 while the pump was in charge



**Fig. 2.** Influent COD and sum of 16 EPA priority pollutant PAH concentrations during all three stages.

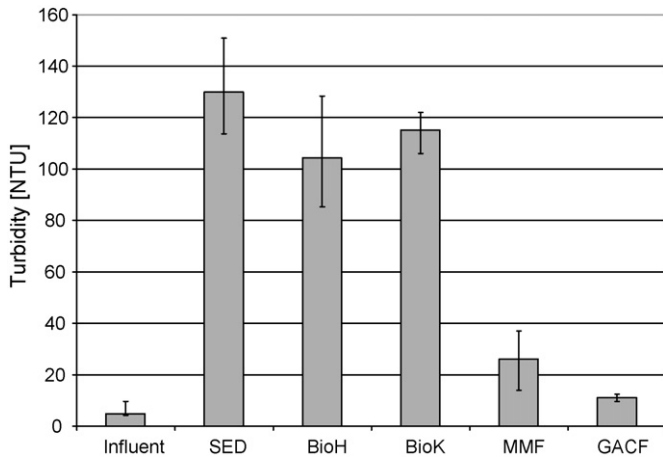


Fig. 3. Turbidity in all process steps.

with minor bounce back effects, when the pumping was suspended for a few days. This is a typical trend also witnessed in other experiments [28]. In stage 3 Well 1 and Well 2 each contribute 50% to the influent; the generally higher concentration of contaminants of Well 2 increased the COD and also the concentration of the other compounds.

3.1.1. General performance of the plant

After the inoculation, sufficient time was provided for the establishment of an appropriate biological activity in the SFFRs. Within the first 40 days, their pressure in the SFFRs increased slightly, indicating biofilm growth. At this time a back flush of the biofilters was performed but the pressure conditions did not change much. Thereafter the pressure was stable throughout the whole duration of the experiment. This date was considered as the end of start-up and the beginning of the test phase. The removal rates of the two different sized SFFRs were marginally different, with BioH offering a higher HRT showing a subtly better performance. But the satisfactory effluent quality in stage 3, at high hydraulic loading, showed that the biological degradation had further capacity.

The groundwater, coming in almost clear at a very low redox potential (ORP) in the range of –260 to –380 mV, turned out to be a difficult matrix. At contact with air in the first process step the turbidity increased greatly and the groundwater became grayish-white. The main reason was the formation of elemental sulfur, but iron and lime precipitates were formed as well and tar like components were observed. A thick grayish floating layer was formed on the sedimentation tank after a few weeks of operation.

The potential chemical mechanism behind the formation of sulfur is a coproportionation between sulfite and sulphide (Eq. (1)). An elementary analysis of the flotite (HEKAtech, CHNSO Analyzer) verified the high content of sulfur, 43.6–74.7% of dry mass, while the carbon content was only 5.4–9.8%.



In the process steps following sedimentation/flotation the turbidity decreased due to particle removal by mechanical filter effects (Fig. 3). Still, turbidity values after the MMF were remarkably high, higher than the turbidity levels usually expected after multi-media filtration.

A back flush of the MMF was done every 2 weeks in stages 1 and 2, in the high flow stage every 3–6 days. The back flush conditions were 2 min air upflow (40 m<sup>3</sup>/h) and 5 min water upflow (32 m<sup>3</sup>/h).

Probably due to the elevated particle concentration after the MMF the pressure drop in the final GACF I increased relatively quickly (80–120 mbar per week) and it had to be substituted by the second GACF II for stage 3.

Clogging effects by sulfur or iron are also reported by other authors when treating groundwater [29]. Over time, the precipitates described herein caused constrictions in pipes and clogging of pumps and they disturbed measurement devices, including flow meters and pH and oxygen sensors. This influenced the stability of the control mechanism for flow regulation and bouncing of the flow rate aroused. The flow fluctuations gradually worsened until a cleaning of the affected pipes and flow sensors was made in stage 2 and the plant returned to good operating conditions. In stage 3 the hydraulic capacity of the pilot plant was close to its limits and a couple of plant shut downs occurred due to different technical failures. Despite the mentioned problems, it has to be noted that the plant

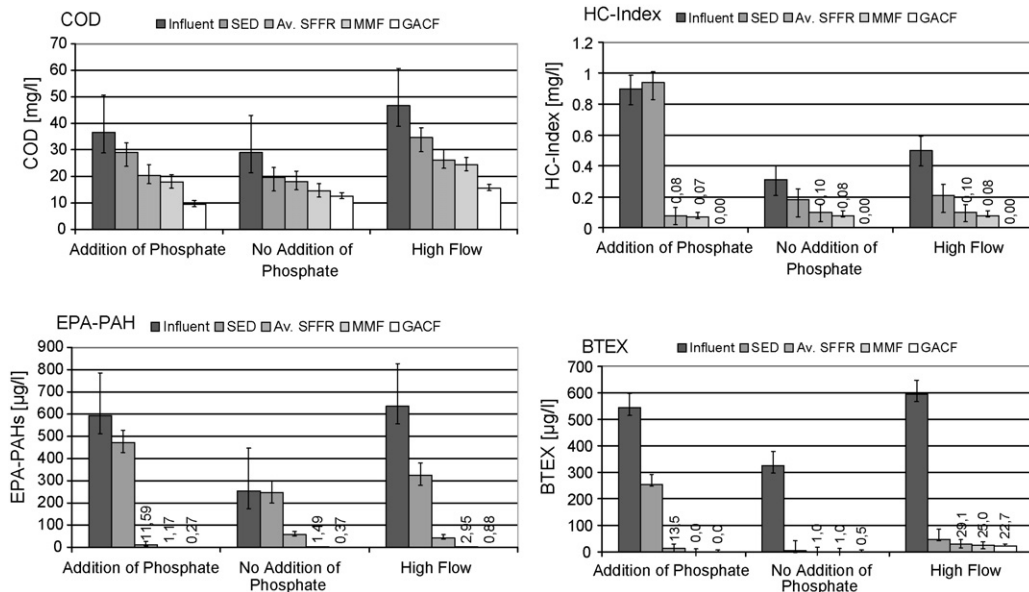


Fig. 4. The removal of COD, HC-index, EPA-PAHs and BTEX. All three stages are shown with an average value for each process step (influent, sedimentation, submerged fixed film reactors, multi-media filter, and granulated activated carbon), bars indicate minimum and maximum values.

**Table 6**  
Qualitative and quantitative analyzes of sedimentation exhaust air

Retention time (min)	Substance	Qualifier for identification (%)	Off gas concentration stage 1/2 (ppm)	Off gas concentration stage 1/2 (ppm)	Mass-fraction
9.7	Benzene	95	190–260	370–500	58.0–78.0 Ø 61.4%
14.5	Ethylbenzene	91	16–34	32–66	4.8–10.0 Ø 8.8%
12.3	Toluene	91	12–17	23–32	3.5–5.0 Ø 4.6%
14.7	<i>o/m</i> -Xylene	91	9–13	16–25	2.5–3.8 Ø 3.4%
15.3	<i>p</i> -Xylene	90	6–7	12–14	1.8–2.2 Ø 2.0%
10.1	Naphthalene	23 <sup>a</sup>	5–7	10–13	1.5–2.0 Ø 1.8%
18.7	Indane	94	5–7	10–13	1.5–2.0 Ø 1.6%
12.6	Not identified	–	5–7	10–13	1.5–2.0 Ø 1.6%
12.7	Not identified	–	3–5	7–10	1.0–1.5 Ø 1.3%
15.9	Isopropylbenzene	94	3–5	7–10	1.0–1.5 Ø 1.2%
13.8	Ethylcyclohexane	49 <sup>a</sup>	2–5	4–11	0.5–1.5 Ø 1.0%

<sup>a</sup> Unsatisfactory identification.

was operated constantly almost throughout the whole investigated period. After 6 months of continuous experiments the SFFRs were opened and the carrier material was inspected. Only in the very bottom layer of the carrier material some deposits of tar components were found. With this regard, the choice of smaller carriers seems not advisable. Smaller carriers provide a higher surface to volume ratio and increased biofilm densities. While the volumetric conversion rate might be enhanced by using smaller size carriers, the filters can also become more prone to clogging.

### 3.2. Removal of organic contaminants

#### 3.2.1. COD

COD is a gross parameter for total organics. The decrease along the course of flow through the plant provides an overview of the performance of the different process steps. Fig. 4 shows that each process step contribute to the removal of COD. The decrease in the sedimentation basin is obviously due to removed sediments and floating particles but the long HRT and the aeration also might allow some biological degradation in this step. The SFFRs fulfilled their expectations quite well and the MMF contributed by retaining eluted biofilm particles and other suspended solids. However, the data also show that a significant percentage of the COD is not eliminated. A residual concentration between 9 and 15 mg/l neither was biodegraded nor absorbed on the activated carbon. Additional

analyses of the BOD<sub>5</sub> proved that the organics, which are readily biodegradable, were removed between 95 and 99%. Influent BOD<sub>5</sub> concentrations between 16.0 and 4.5 mg/l (average 10.5 mg/l) were degraded to 0.8 and 0.1 mg/l (average 0.4 mg/l). A comparison with the MGP site Griftpark [23] shows, that their influent COD of 115 mg/l is almost twice as high as the maximum COD influent of this site (61 mg/l), on the other hand the average removal efficiencies herein are slightly better than their achievements (42–50%), even the HRT at Griftpark plants is twice as long.

#### 3.2.2. HC-index

The HC-index measures the sum of hydrocarbons which are a major target of purification efforts. The results shown in Fig. 4 indicate that the SFFRs achieve significant removal of contaminants. Even during the high flow stage the residual HC concentration is below 0.1 mg/l. This reconfirms the good biodegradability of the hydrocarbons. The following MMF does not contribute much, but the GACF absorbs the residual HC below detection limit (0.03 mg/l). Oesterholt et al. confirm the good bioavailability of hydrocarbons. Mineral oil concentrations of even 9.5 mg/l get degraded to 94% (HRT = 2 h) [23].

#### 3.2.3. EPA-PAHs

The analysis for aromatic compounds focused on the 16 EPA priority pollutant PAHs, representative for a class of carcinogenic

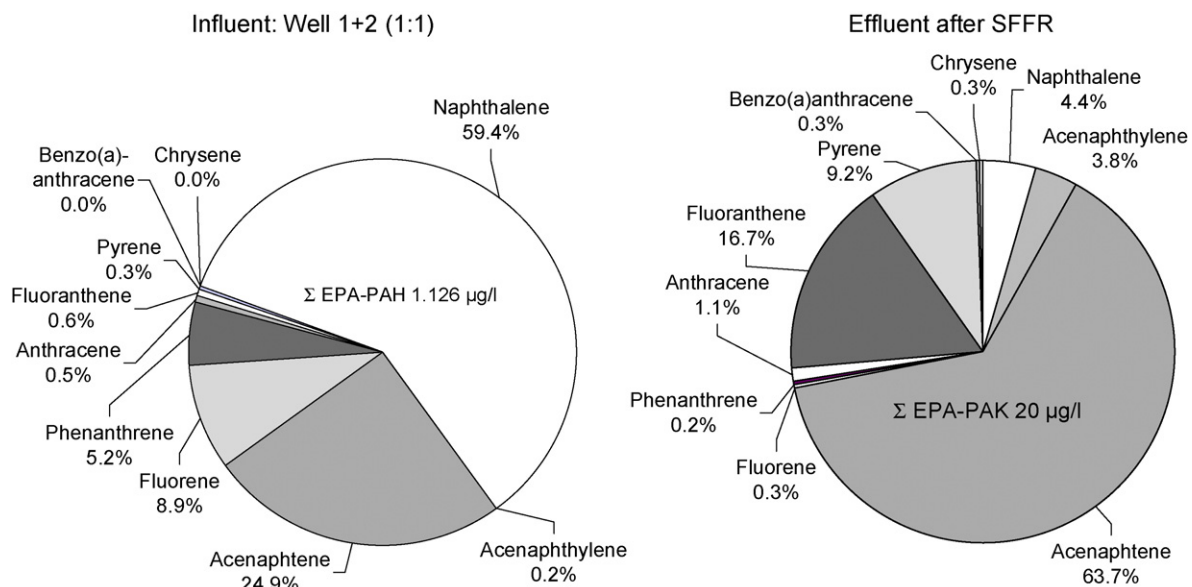


Fig. 5. Distribution of PAHs in influent (Well 1 + Well 2, 1:1) and in effluent.

and mutagenic substances. PAHs of higher molecular weight are more toxic, but the lower molecular weight compounds are more soluble in the groundwater and thus have a greater potential to reach receptors [18]. The transport of PAHs is complex, since it not only depends on water solubility, but these compounds can also be transported as colloids or adsorbed to humic acids [30]. Two or three ring PAHs are biodegraded readily while compounds containing more than four rings, are biodegraded cometabolically, with other compounds acting as growth substrates [31]. Low solubility of complex PAHs reduces their bioavailability and makes biodegradation difficult resulting in their persistence in contaminated sites [32].

In the investigated case the concentration of PAHs in groundwater with a higher ring number than four were below or close to the detection limit (0.03 µg/l). The distribution pattern of PAHs in Well 1 and Well 2 were significantly different. In Well 1 (561 µg/l EPA-PAHs) located close to the tar disposal site, 49% of the PAH content was acenaphthene. In Well 2 (1692 µg/l EPA-PAHs), located near the former naphthalene scrubber, 75% of the PAHs was naphthalene. Similar to the other hydrocarbons, PAH concentrations were highest immediately after implementing a new well and exhausted while the wells were pumped.

Both influent qualities could be treated successfully in the SFFRs with removal rates between 77 and 98%. Fig. 5 gives an example of the distribution of PAHs in the inlet and the outlet of the SFFR. Naphthalene, being the smallest PAH, proved to be 100% available for biodegradation. Acenaphthene was slightly more persistent, which lead to a relatively higher share in the PAHs present in the effluent. Residual concentrations of PAHs were almost completely adsorbed in the subsequent activated carbon treatment. Including the GACF the removal rate in all stages was beyond 99.5% with total levels in the range from 0.27 to 0.88 µg/l. These results are confirmed by other authors. Findings in Griftpark show comparable influent concentrations and removal rates [22], while Guerin [12] treats a much higher concentration (total PAH = 120 mg/l) successfully with 99.8% removal, at a HRT of 3.5 h [4].

In previous experiments in a similar application [33] it was demonstrated that PAHs are not only adsorbed in the GACF but also undergo microbial degradation. The occurrence of aerobic biological activity is supported by the observed oxygen consumption in the GACF. By this effect, termed bioregeneration, the lifetime of a GAC filter can be extended and the activated carbon require less frequent regeneration [34,35]. At the end of the experiments from both GAC filters several samples of the activated carbon at different filling levels were taken and the residual iodine adsorption capacity was determined. From these analyses and the total volume of groundwater treated in each GACF, the maximum treatment capacity of the activated carbon was calculated. For both filters, a similar capacity of 24,000 m<sup>3</sup> groundwater per m<sup>3</sup> activated carbon was determined.

### 3.2.4. BTEX

BTEX are highly volatile toxicants, corresponding to their higher Henry's law constant compared to other hydrocarbons [36] and get easily stripped by aeration [22]. Therefore most of the BTEX were removed in the aerated sedimentation/flotation unit. In order to verify this, the sedimentation and the SFFRs were sealed and the exhaust air was analyzed by gas chromatography (GC). A flame ionization detector (FID) was used for the exhaust air analysis. Organic carbon was found in the range of 96.3% (stage 1 + stage 2) and 95.6% (stage 3) of the organic carbon represented by BTEX in the influent water. A quantitative analysis using a sequential purge-and-trap analysis with MS detector proved, that these organic exhaust gases consisted mainly of BTEX, with a benzene concentration of >58%, while other substances as, e.g. naphthalene were not much present.

**Table 7**  
Results of analysis of phenolic compounds (average of  $n \geq 3$  samples)

Sample	Sum (µg/l)	Phenol (µg/l)	o-Cresol (µg/l)	p-Cresol (µg/l)	2-Ethylphenol (µg/l)	2,6-Dimethylphenol (µg/l)	2,5-Dimethylphenol (µg/l)	2,4-Dimethylphenol (µg/l)	3,5-Dimethylphenol + 4-ethylphenol (µg/l)	2,3-Dimethylphenol (µg/l)	3,4-Dimethylphenol (µg/l)	2,3,5-Trimethylphenol (µg/l)	2,4,6-Trimethylphenol (µg/l)	3,4,5-Trimethylphenol (µg/l)	2-Isopropylphenol (µg/l)	4-Isopropylphenol (µg/l)
Well 1 influent	296.1	<0.5	5.6	4.2	<0.5	5.5	20.9	55.0	65.1	25.1	28.3	12.5	8.8	2.2	8.1	39.3
SED effluent	265.0	6.7	40.5	22.7	5.3	10.2	16.3	37.3	50.3	20.6	10.1	13	12.1	1.8	1.7	11.9
SFFR BioH effluent	184.8	7.9	20.5	11.9	3.1	6.7	10.6	26.0	42.9	14.4	7.6	8.9	8.0	1.3	0.7	11.9
SFFR BioK effluent	232.1	8.3	31.5	18.0	4.1	8.3	13.4	32.0	51.1	17.6	9.1	10.8	9.7	1.6	1.4	12.0
GACF effluent	7.2	<0.5	<0.5	6.3	<0.5	<0.5	<0.5	<0.5	0.9	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5

Results for *m*-cresol, 3-ethylphenol and 4-ethylphenol, 2-propylphenol and 4-propylphenol, 2,3,6-trimethylphenol, 3-isopropylphenol, 2-propylphenol, and 4-propylphenol are not listed because concentrations were below the detection level of 5 µg/l.

The identified substances listed in Table 6 comprise more than 90% of the total organic C present in the off gas. The GC–MS analyses brought not only a satisfactory identification of the substances, but also quantitative data, which fit very well to the TOC balance. The results proved that BTEX are almost completely removed by stripping and no biological degradation was observed. While no exhaust air treatment was installed at the pilot plant, a major plant would certainly require one to trap BTEX. Adsorption on activated carbon is probably the most convenient technology. Other studies [4,23] show very promising results for biological removal of BTEX.

### 3.2.5. Phenols

Phenols were analyzed according to DIN 38 409 where three different methods are described: method H16-1 employing extraction of phenols with an organic solvent, H16-2 consisting of a distillation and an extraction step, and H16-3 done by distillation only. The results of these three methods were significantly different (e.g. for a sample from Well 1: 0.48, 1.05, and 0.65 mg/l). The reasons might be the interference of certain contaminants to the color reactions on the one hand; on the other hand the cracking of larger molecules with hydroxyl groups during distillation, which are later detected as phenols. To clarify the picture, samples were sent to the Geoscience Center Goettingen, Germany, a university laboratory specialized in phenol analytics. Their detailed results proved that the sum concentration of phenolic compounds of both Well 1 and Well 2 were around 300–500 µg/l and they were reduced to 5–10 µg/l in the GACF effluent. This is in accordance with other findings [22]. While the concentration of phenol itself is low, several other compounds have higher concentrations (Table 7). Substances with concentrations <5 µg/l (e.g. *m*-cresol) are excluded of the table. Therefore, phenols can be considered an uncritical parameter in this groundwater.

### 3.3. Removal of other contaminants

The concentration of total cyanides found in the influent was 0.5–0.7 mg/l. Total cyanides proved to be inert and no significant degradation was observed in the process steps. Also on other sites, cyanide appeared not to be accessible for any treatment, since it is present in complexes [22]. The reason is that cyanide compounds found at former MGP sites mainly occur as relatively nontoxic iron-complexed forms, such as ferric ferrocyanide, rather than the highly toxic free cyanide forms. The determination of cyanides in MGP site

cleanup is due to misunderstanding, that not all chemical forms of cyanide are highly toxic, e.g. ferric ferrocyanide, also known as Prussian blue, is a widely used coloring agent of low toxicity [37]. Moreover, the chemical conditions at most former MGP sites limit the extent to which free cyanide may be released into air and water from complex cyanides [38]. According to Shifrin et al., there is little, if any concern for either ingestion or dermal contact exposures to any form of cyanide potentially present in soil at former MGP sites [38].

The Austrian legal requirements for discharge into water bodies have no regulation for total cyanides, but easily purgeable (=free) cyanides are limited with less than 0.1 mg/l. This requirement could be achieved with effluent concentrations mostly below the detection limit (0.01 mg/l).

Ammonium was found in concentrations between 3.1 and 7.2 mg/l, while oxidized N components were not present. Part of ammonium was consumed during biological conversion of the organic compounds but still more than 50% of the ammonia was left in the effluent. Nitrification in the SFFRs was not observed or only to a very small extent, probably due to the low temperature and the low HRT.

Sulfide was detected in significant concentrations in the range of 3.1–17.6 mg/l. The actual concentration in the groundwater was presumably even higher but at contact with air, sulfide was rapidly oxidized and the concentration in the effluent was very low (<0.08 mg/l).

Heavy metal ions were analyzed only monthly, since their concentrations were insignificant, far below the treatment requirements.

### 3.4. Comparison of the performance in the different stages of investigation

In stage 1 the effluent quality met all expectations, in particular the limits of direct discharge into open water bodies. The quality came even close to the very stringent standards set within the Austrian Groundwater Quality Monitoring Ordinance, which are established to guard groundwater resources that are a major source of drinking water in Austria (Table 8). Usually such high standards can be only achieved involving advanced treatment technologies such as ozonation or UV/peroxide treatment.

In stage 2 the necessity for phosphorous supplementation should be clarified. Nutrients are essential for efficient degradation

**Table 8**  
Summary of the effluent parameters, compared to Austrian legal requirements

Parameter	Disposal into sewerage system	Disposal into public water bodies	Groundwater threshold value ordinance	Effluent stages 1 and 2 (average)	Effluent stage 3 (average)
PAH	–	100 µg/l (16-EPA <sup>a</sup> )	0.1 µg/l (6-PAH <sup>b</sup> )	0.27 µg/l (16-EPA)	0.88 µg/l (16-EPA)
Benzene	–	–	0.1 µg/l	<0.1 µg/l	<0.1 µg/l
BTEX	100 µg/l	100 µg/l	Limited for benzene and toluene; 0.1 µg/l each	<0.1 µg/l	11.4–34.0 µg/l
Phenols	20 mg/l	0.1 mg/l		<0.01 mg/l <sup>c</sup>	0.76 mg/l <sup>c</sup>
Cyanides (easily purgeable)	0.5 mg/l	0.1 mg/l	0.03 mg/l (total cyanides)	≤0.05 mg/l	0.22 mg/l
TOC		25 mg/l		3.6–5.8 mg/l	6.4–8.7 mg/l
COD	–	75 mg/l	–	8.1–13.4 mg/l	13.9–24.1 mg/l
HC	20 mg/l	10 mg/l	0.06 mg/l	<0.1 mg/l	<0.1 mg/l
NH <sub>4</sub> -N	–	10 mg/l	0.03 mg/l	4.6–7.5 mg/l	6.2–9.5 mg/l
NO <sub>2</sub> -N	–		0.01 mg/l	0.0–0.5 mg/l	0.0–0.1 mg/l
Fe				0.22–0.34 mg/l	0.42–0.55 mg/l
Mn	10 mg/l	1.0 mg/l		0.18–0.20 mg/l	0.22–0.23 mg/l
S <sub>2</sub> <sup>-</sup>	–	2.0 mg/l	–	<0.08 mg/l	<0.08 mg/l

<sup>a</sup> Sum of benzo(a)pyrene, fluoranthene, benzo-(b)-fluoranthene, benzo-(k)-fluoranthene, benzo-(ghi)-perylene, inden-(1,2,3-cd)-pyrene.

<sup>b</sup> Sum of 16 PAH congeners according to EPA.

<sup>c</sup> HS-SPME–GC–MS according to a new DIN-method, which is under way.



of organic HC compounds. As a general rule, in aerobic degradation the optimum relation of COD:N:P is estimated by 200:5:1. A maximum of about 61 mg/l COD therefore needed 1.5 mg/l N and 0.3 mg/l P. Such, the concentration of  $5(\pm 2)$  mg/l  $\text{NH}_4\text{-N}$  was more than sufficient. This was not the case for phosphorous. Since the detected phosphorus-levels were only around 0.05 mg/l, phosphorus was added in the form of diluted phosphoric acid by membrane pump. A concentration of 0.5 mg/l P was set, in order to clearly avoid a P-limitation. On the other hand, remaining P might also cause problems, e.g. pond treatment as a final polishing step was considered where elevated P levels might stimulate algal growth. As well it was suspected that remaining P might enhance biological activity in the soil after re-infiltration, which would then lead to problems due to clogging of infiltration wells. Therefore the addition of P was seen ambivalent. To investigate the requirement for P supplementation, the second experiment stage was conducted without the addition of phosphorus. The removal results for core contaminants were similar and no significant loss of performance was observed. It was concluded that phosphorus was not a limiting factor in this case. One reason was, that approximately 50% of the organic contaminants were removed by physical process steps (sedimentation, flotation, stripping, and filters). Therefore the addition of phosphorus was not resumed. However, such a decision should not be taken easily and not only the concentrations of pollution but also the remediation concept has to be considered.

In the final experimental stage (stage 3) the hydraulic load was doubled to check the limits of plant performance. As it can be taken from Table 1, under these conditions the effluent quality did not meet all criteria for discharge into open water bodies but it was still sufficient for disposal into the sewage system.

#### 4. Conclusions and recommendations

The investigated pilot plant setup provided valuable field experience for a full-scale plant. At a flow rate of 1 l/s high effluent quality could be achieved, meeting the Austrian legal requirements for discharge into public water bodies, which was a main treatment goal. At double flow rate the effluent quality worsened. Still the requirements for discharge into public water bodies were achieved except for the cyanide concentration. Appropriate pre-treatment turned out to be a critical issue to achieve good results and to maintain stable operating conditions. The first treatment step should have a sturdy construction, which can be easily maintained, and it should allow simple removal of floatable or settleable precipitates. A HRT >3 h is recommended to provide sufficient time for completion of precipitation reactions in order to protect the following reactors from clogging.

The selection of the reactor configuration for biological treatment is a critical point. Exhaust air treatment, filling material and backwashing have to be considered. The chosen system turned out to be highly reliable and the SFFRs contributed much to the degradation of the typical MGP contaminants. As another recommendation, it is suggested for the full-scale plant to establish a counter-current flow regime instead of the applied co-current flow. This would leave tar precipitations at the top layer where they can be easily removed. Furthermore the aeration devices at the bottom would not be affected by deposits as observed in the pilot plant.

The addition of phosphate showed no clear evidence of improved biological removal of contaminants, even while the COD:N:P ratio might suggest so. However, as discussed before, the necessity of nutrient dosage should be assessed in each individual case.

The MMF exhibited a certain deficit in protecting the GACF from particles from the SFFRs. The reason is presumably the break-

through of finely dispersed sulfur precipitates through the MMF. With regard to the observed pressure increase also the GACF should be equipped with a back flush option. Nevertheless, the final GACF fully assured the effluent quality and the residual concentrations of the target contaminants were close to detection level.

In summary the investigated pump-and-treat system proved to be an efficient and cost-effective means of hydraulic containment and groundwater protection. This concept as presented above is currently implemented in the design of a full-scale treatment plant.

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